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# INDUSTRIAL AND ENGINEERING CHEMISTRY

## ANALYTICAL EDITION

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# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Determination of Manganese, Nickel, and Phosphorus in Iron and Steel

### The Use of Rapid Spectrophotometric Methods

W. M. MURRAY, JR., AND S. E. Q. ASHLEY, General Electric Company, Pittsfield, Mass.

The authors present methods for the rapid photometric determination of manganese, nickel, and phosphorus in iron and steel.

From four to six determinations of any of the elements mentioned may be run with checks in an hour and the speed of single determinations is almost as great as for a group.

No standard solutions are required, and any instrument may be quickly calibrated with two or three determinations within the limits mentioned.

The reproducibility of the determinations is high, and judging from the results obtained on Bureau of Standards samples the accuracy is as good or better than is obtained with most routine determinations.

THE development in recent years of various types of instruments for the quantitative measurement of the degree of absorption of visible light in solutions has vastly enlarged the domain of chemical colorimetry by substituting accurate absolute measurements for crude comparisons of the color of solutions. Excellent review articles by Mellon (6) and Strafford (13), describing these instruments and pointing out their advantages, have appeared during the last year. One of the great advantages of a spectrophotometer is that it is a selective instrument and permits the determination by the absorption of a chemical constituent even in the presence of another colored compound which would mask or pervert the color of the solution so much as to make an ordinary color comparison impossible. One very important application of this advantage immediately comes to mind in the rapid analysis of ferrous alloys, and it is this field which the present authors have investigated for spectrophotometric exploitation.

Most absorption bands are rather broad, so that for practical purposes it is sufficient to employ an instrument which

isolates the various regions of the spectrum by means of filters transmitting a narrow band of light. Such an instrument is the Zeiss Pulfrich step-photometer which was used in the present investigation. The construction of this instrument is too well known to warrant description, but may be found in any of the Zeiss Company's literature (15).

A survey of the literature showed that the problem which was undertaken had already been treated in part by other investigators, mostly in Germany, and much of it is too recent to have been tested by other workers. The task at hand became that of testing some of the methods which have already been developed and improving some of the older methods which have not proved sufficiently reliable by the older colorimetric technique.

The methods selected were those for manganese, nickel, and phosphorus, based on requirements of local foundry work as well as their chemical adaptability for the purpose in mind.

#### Technic

All photometric measurements were made with the Zeiss Pulfrich step-photometer. The general technic employed in making the measurements was that described in the directions which accompany the instrument. The extinction,  $k$ , was read directly from a calibrated drum on the photometer. The extinction coefficient,  $K$ , was then obtained by dividing  $k$  by  $s$ , the length of the cell used.

$$K = \frac{k}{s} \quad (1)$$

It is thus possible to cover a wide range of concentrations by using cells from 0.5 to 5 cm. in length, and have all measurements reduced to the common basis of a 1-cm. cell length.

Calibration graphs were plotted with per cent of constituent and extinction coefficient,  $K$ , as coordinates. The graphs in each case were straight lines, so that a simple equation for the per cent of the constituent  $X$  may be derived from the slope of the line.

$$\% X = \frac{K}{c} \quad (2)$$

The constant  $c$  is specific for a given procedure, and once determined will always hold for that particular method.

It has thus been found expedient to use these equations for routine work since they are much simpler and less liable to



error in interpretation than calibration graphs. In some instances graphs will be given as illustration of typical results in the work which is to follow.

### Manganese

There are many procedures for the colorimetric determination of manganese in iron and steel. Mehlig (5) has studied a spectrophotometric method using a procedure depending upon preliminary precipitation of manganese dioxide and subsequent oxidation of the separated manganese with sodium bismuthate. Müller (9) has pointed out that such separations are probably not necessary and that equations employing the extinction coefficient are very reliable. In a review of photoelectric colorimetry, Müller (10) gives a calibration graph for pure permanganate solutions which were oxidized by a periodate procedure, but neither details of the procedure nor applications were given.

TABLE I. SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE  
(Synthetic and Bureau of Standards samples)

Sample	$k$	Cell Length Cm.	$K$	Manganese Found %	Manganese Present %
1	0.30	3.0	0.10	0.05	0.04
2	0.94	3.0	0.31	0.15	0.14
3	1.09	1.0	1.09	0.54	0.53
4	0.75	0.5	1.50	0.75	0.75
5	1.26	0.5	2.52	1.26	1.27
51 <sup>a</sup>	0.52	1.0	0.52	0.26	0.27
51 <sup>a</sup>	0.25	0.5	0.50	0.25	0.27
55 <sup>a</sup>	0.13	3.0	0.04	0.02	0.019
10c <sup>a</sup>	1.15	0.5	2.30	1.15	1.13
5f <sup>a</sup>	0.77	0.5	1.54	0.77	0.76

<sup>a</sup> 51, 55, 10c, 5f are Bureau of Standards samples.

In the work described here, the periodate procedure of Willard and Greathouse (14) was used for oxidizing the manganese. This procedure has been noted as a superior means for oxidizing manganese to permanganic acid, but it does not lend itself easily to use in titration methods, as it is not easy to destroy the excess of periodate without destroying the

permanganate at the same time. The advantage of the method lies in the rapidity, accuracy, and stability of permanganate, and as no separations are involved, the procedure is very simple. The stability of the permanganate absorption band has been studied many times (7) and it has been found that it does not shift appreciably with changes in concentration or cation.

**PROCEDURE.** Weigh 0.500 gram of the iron or steel sample, and transfer to a 150-ml. beaker. Dissolve in a mixture of 15 ml. of concentrated nitric acid and 25 ml. of water, heating on a hot plate to hasten solution. When the sample is dissolved, add 20 ml. of water, filter, and wash with small portions of water. To the clear filtrate add 10 ml. of concentrated sulfuric acid and a small lump of ammonium persulfate. Boil for 10 minutes. Cool slightly, and add 10 ml. of 85 per cent phosphoric acid and approximately 0.5 gram of potassium periodate. Boil for 1 minute, and keep hot (90° C.) for 10 minutes. All heating and boiling should be done in an open beaker to keep the volume down. Cool to room temperature by placing in a pan of cold water, then dilute to exactly 100 ml. in a volumetric flask. The extinction coefficient of the clear permanganate solution is then determined, using distilled water as a comparison liquid. The measurement is made with a green filter with mean transmission at 5300 Å., since this is in the region of maximum absorption for the permanganate ion (3, 4).

**RESULTS.** Calibration graphs prepared from pure manganous sulfate (from c. p. potassium permanganate) and ferric nitrate (from Bureau of Standards ingot iron) solutions gave straight lines passing through the origin. This means that the effect of iron is negligible in the presence of the large excess of phosphoric acid present. The range covered is from 0.01 up to about 1.5 per cent of manganese. The accuracy is of the order of 0.01 per cent of manganese. The calibration equation derived for this procedure was

$$\% \text{ manganese} = \frac{K}{2} \quad (3)$$

The data in Table I are typical and serve to illustrate the results obtained by dividing  $K$  by the constant 2 as found from the calibration graph and given in the calibration equation (3). This calibration equation applies only to this specific procedure and photometer, but similar equations can be derived for other photometers with only one or two measurements on standard solutions, as the procedure has been found reliable and reproducible.

### Nickel

Rollet (11) studied the colorimetric determination of nickel in cobalt salts, nickel steels, and organic matter. The method depends on the formation of a soluble nickelic dimethylglyoxime. It was found that iron hydroxide tends to drag down small amounts of nickel hydroxide in ammonia precipitation, and this was avoided by adding dimethylglyoxime to form the nickel complex before the ammonia is added. Recently Dietrich and Schmitt (1) have used a modification of this procedure in the development of a rapid photometric method for nickel in iron and steel. It is inferred that iron was separated by ammonia precipitation, although the treatment is not mentioned specifically. The iron must be either removed or held in solution as a complex, since the nickelic complex is formed in alkaline solution.

In the procedure developed in this study, the iron is held in alkaline solution by adding a large excess of citric acid. This alkaline iron citrate solution has a light yellow color. The nickel dimethylglyoxime solution is a deep wine-red color. Absorption curves for these solutions are given in Figure 1. It is obvious that the iron has practically no absorption in the visible region of the spectrum above 5000 Å. On the other hand the nickel shows a plateau in its absorption band near 5300 Å. Therefore, if the photometric measurements are made using a filter with mean transmission at 5300 Å., the

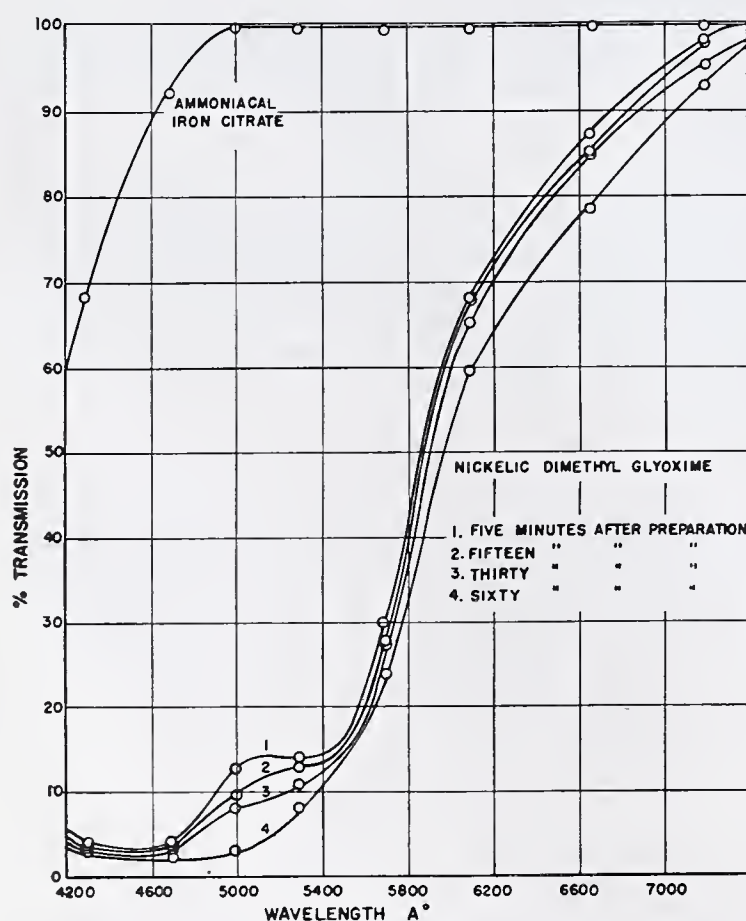


FIGURE 1



absorption of the iron will be eliminated entirely and a preliminary separation becomes unnecessary.

Dietrich and Schmitt (1) found the absorption curve of the nickelic dimethylglyoxime solution to be stable for eight hours. As is evident from Figure 1, such was not found to be the case in this work. The freshly prepared solutions (curve 1) show an absorption plateau in the region of 5300 Å. The first curve taken immediately after mixing the reagents corresponds to the curve given by Dietrich and Schmitt. Curves 2, 3, and 4 show that this plateau rapidly disappears, and after the solution has stood for an hour the absorption curve shows only a single wide and smooth band. These curves were all prepared from pure nickel solutions, but it was found that the same curves were obtained when citric acid was present. Although the Pulfrich photometer used gives only eight points on the curves, their general shape has been confirmed on a General Electric spectrophotometer which automatically records a smooth line from a monochromator whose slit emits a band only 100 Å. in width.

The reason for the appearance of this plateau and its rapid change has not been ascertained, but it has been found to be reproducible and measurements completed within 10 minutes after mixing the reagents give consistent and reliable results.

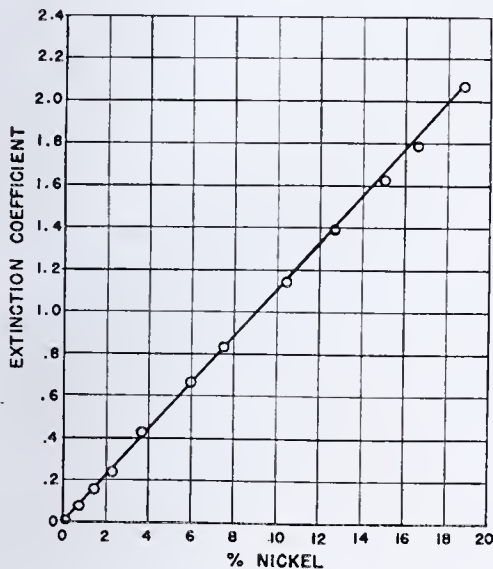


FIGURE 2

**PROCEDURE.** Weigh 0.400 gram of the iron or steel and transfer to a 1000-ml. volumetric flask. Add 25 ml. of 1 to 1 nitric acid and warm on a hot plate until the sample is dissolved. (In some cases of difficultly soluble chromium-nickel steels, a mixture of equal parts of nitric and hydrochloric acids may be necessary.) When solution is complete, cool and dilute to 1000 ml. Mix thoroughly and allow to stand for 5 or 10 minutes so that any graphitic carbon and silica may settle to the bottom. Pipet exactly 25 ml. of the clear supernatant solution into a 100-ml. volumetric flask. Then add the following reagents to the small sample in the order given and with thorough mixing after each addition: 10 ml. of citric acid solution (10 per cent), 5 ml. of saturated bromine water, 5 ml. of 1 to 1 ammonium hydroxide, and 3 ml. of a 1 per cent solution of dimethylglyoxime in alcohol. Dilute the contents to exactly 100 ml. with distilled water and again mix thoroughly. The solution should be clear and a deep red color. The photometric measurements must be made within 10 minutes after the addition of the reagents. The measurement is made with a green filter with mean transmission at 5300 Å.

**RESULTS.** Pure solutions of iron (from Bureau of Standards sample 11d) and nickel (from Hilger H. S. brand nickel rod) nitrates were used in preparing the calibration graph which is given in Figure 2. The line is satisfactory, showing a maximum error of about 0.2 per cent nickel in the higher concentrations and about 0.05 per cent nickel in the lower concentrations. The range covered is from 0.5 to 19 per cent nickel.

The limit of usefulness of the method for high nickel concentrations is determined by the solubility of the complex. If samples containing over 20 per cent nickel are analyzed by this method, a precipitate forms rather quickly and the results are of no value. It is possible, however, to start with a smaller sample and calculate the results back to the basis of a 0.400-gram sample as used.

TABLE II. SPECTROPHOTOMETRIC DETERMINATION OF NICKEL

Sample No.	B. of S. No.	Cell Length Cm.	(Bureau of Standards samples)		Nickel Found %	Nickel Present %
			k	K		
1a	107	3.0	0.275	0.091	0.83	0.807
b	107	3.0	0.275	0.091	0.83	0.807
2a	33a	1.0	0.36	0.36	3.27	3.24
b	33a	1.0	0.37	0.37	3.36	3.24
3a	32b	3.0	0.41	0.14	1.27	1.20
b	32b	3.0	0.40	0.13	1.18	1.20
4	101	1.0	0.945	0.945	8.60	8.44
5	115	0.5	0.87	1.74	15.83	15.89

The data in Table II show the results obtained on the analysis of Bureau of Standards samples by this method. The agreement is satisfactory for routine foundry analyses, and the time saved by using the photometric method is considerable. The values for the per cent of nickel found were obtained from the calibration equation, which was derived from several values from the calibration graph and was found to be

% Ni = 9.10 × K

(4)

Phosphorus

The determination of phosphorus in iron and steel samples has always been a tedious and time-consuming task. The many methods in use are practically all based on some modification of a method involving preliminary precipitation of ammonium phosphomolybdate. The question always arises as to how complete this precipitation can be made, how definite is the composition of the salt, and how reliable are the subsequent methods of treatment of the salt after it is obtained. Very good results can be obtained by these standard procedures in the hands of a skilled operator; however, most of them are open to many errors and a quicker and less tedious method is desirable.

Of the older colorimetric methods for determining phosphorus in iron and steel, the one worked out by Misson (8) appeared to be most worth studying. It has been used and found satisfactory by Schröder (12) and Getzov (2), but does not seem to have been given any widespread use. This method depends on the formation of a yellow phosphovanado-molybdate, whose formula is (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>·NH<sub>4</sub>VO<sub>3</sub>·16MoO<sub>3</sub> according to Misson (8). It was found to be a stable complex, showing almost no color change after 14 days' standing. The accuracy claimed for the method was 0.005 per cent of phosphorus in the range 0.04 to 0.1 per cent of phosphorus. All of this work was done using the old method of visual comparison with standard solutions.

This method has been studied in the present work with consideration of the effect of concentration of reagents, acid concentration, and temperature at the time of making the photometric readings. Since the solutions are yellow in color, it is rather difficult to make accurate visual comparison with standard solutions, and slight differences in concentration are not readily detected by the eye alone. The method depends largely on using an acid concentration which is optimum for color formation, and which is different from that used in the original procedures. The method using this new procedure and using the Pulfrich photometer gives very satisfactory results for the range 0.01 to 1.0 per cent of phosphorus.



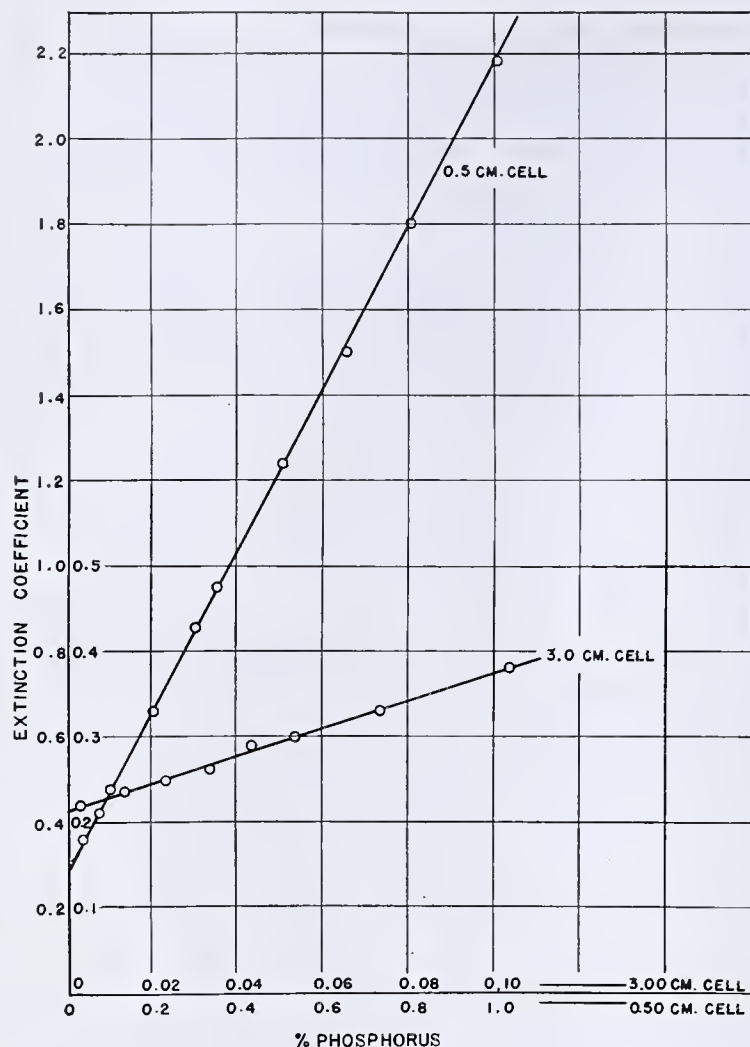


FIGURE 3

Preliminary experiments showed that the acid concentration and the size of sample used in the Misson (8) procedure gave rather erratic results. It was found that the limit of the phosphorus concentration is about 5 mg. per 100 ml. of final volume and higher concentrations tend to give a precipitate. Misson used a 1.0-gram sample of iron, but it was found that a 0.50-gram sample was sufficient and 5 mg. of phosphorus correspond to 1 per cent of a 0.50-gram sample, thus increasing the range of the method. In the older procedure the sample was dissolved in 20 ml. of 1 to 1 nitric acid. The complex is rather sensitive to acid concentration above a certain minimum, so that it is advisable to work with as small amount of acid as is feasible. This was found to be 20 ml. of 1 to 2 nitric acid used to dissolve the sample with a final volume of 100 ml. The effect of acid is illustrated in Table III.

As is evident from the data in Table III, a precipitate forms when the acid concentration is too low. In the case where 40 ml. of acid were used, the color was very slow in forming and the extinction coefficient tended to drift towards higher values as the solution was allowed to stand. Several experiments of this type proved that a maximum color is developed in solutions which are low in acid content, so that it is desirable to work with the minimum of acid present. This is limited, however, by the requirement that a certain amount must be present to prevent the formation of a precipitate.

When readings are taken with the solution at a temperature of 10° C., the values for the extinction coefficient are low, while if the temperature is very high (50° C.), the extinction coefficient tends to be high. It was found that anywhere in the range 20° to 30° C., the readings were almost identical and temperature is unimportant in this small range which covers the usual room temperature.

With these limitations in mind, the following procedure was devised as being best fitted for the phosphorus determination.

**PROCEDURE.** Dissolve a 0.500-gram sample in 20 ml. of 1 to 2 nitric acid with heating. Filter off any silica or graphitic carbon residue, washing with small portions of water. Heat the clear solution almost to boiling, add 5 ml. of 1 per cent potassium permanganate solution and keep the solution just below the boiling point for 10 minutes. Then cool the solution somewhat and add 2 drops of 30 per cent hydrogen peroxide (less than 0.001 per cent phosphorus content). Add exactly 10.0 ml. of ammonium vanadate solution from a pipet. (This solution is prepared by dissolving 2.345 grams of ammonium vanadate in 500 ml. of hot water, adding 20 ml. of 1 to 1 nitric acid, and diluting to 1000 ml.) Heat the sample again to destroy the excess hydrogen peroxide, then place it in a pan of cold water and cool to room temperature. At this point it should be clear and almost colorless. Transfer the solution to a 100-ml. volumetric flask, add 10 ml. of 10 per cent ammonium molybdate solution, and shake thoroughly to dissolve the precipitate which forms momentarily. Dilute to exactly 100 ml. and allow to stand for 10 minutes before making the photometric measurements. The extinction coefficient is measured with a violet filter with mean transmission at 4300 Å. A 3.0-cm. cell is used for samples containing 0.01 to 0.1 per cent phosphorus, and a 0.50-cm. cell for samples containing 0.1 to 1.0 per cent phosphorus.

**RESULTS.** Pure solutions of iron nitrate from Bureau of Standards ingot iron and c. p. potassium phosphate were used in the preparation of the calibration graphs, which are given in Figure 3. It was found that the values of  $K$ , the extinction coefficient for a 1.0-cm. cell, were not the same when using cells of different lengths on the same solution. The values of  $K$  decrease as the cell length is increased from 0.5 to 3.0 cm., and when values of  $K$  are plotted against cell length, a straight line is obtained. However, this is an error of the instrument and not of the method or this particular solution, for similar results were obtained with potassium chromate, picric acid, and ferric chloride solutions. All these solutions show a maximum absorption in the 4300 Å. range, so that it is apparently an effect peculiar to this region which was not observed when working with the nickel and permanganate solutions using the 5300 Å. filter. Because of this effect, two calibration curves and equations were prepared, one using a 3-cm. cell for low concentrations and the other using a 0.5-cm. cell for the higher concentrations.

The equations derived from the two calibration graphs were:

$$\% \text{ phosphorus} = \frac{K - 0.28}{1.90} \text{ for 0.5-cm. cell} \quad (5)$$

$$\% \text{ phosphorus} = \frac{K - 0.22}{1.50} \text{ for 3.0-cm. cell} \quad (6)$$

The term subtracted from  $K$  in the numerator of each equation is the value of  $K$  at zero phosphorus concentration. These solutions contain ferric nitrate which shows a small absorption and they also contain an excess of vanadic acid which also shows a small absorption in the region of measurement. However, this absorption is relatively constant and does not interfere with the measurements.

TABLE III. EFFECT OF ACID CONCENTRATION ON EXTINCTION COEFFICIENT OF PHOSPHOVANADOMOLYBDATE SOLUTIONS

(Samples containing iron with 0.35 per cent of phosphorus, using a cell of 0.50-cm. length in each case)

1 to 2 HNO <sub>3</sub> Ml.	$k$	$K$
15 <sup>a</sup>		
20	0.48	0.96
25	0.47	0.94
40	0.41	0.82

<sup>a</sup> Precipitate formed quickly.

The results obtained in the analysis of Bureau of Standards samples by this procedure are given in Table IV. The values for the per cent of phosphorus found were calculated from calibration equations 5 and 6.



TABLE IV. SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS

Sample No.	Cell Length Cm.	(Bureau of Standards samples)			
		<i>k</i>	<i>K</i>	Phosphorus Found	Phosphorus Present
				%	%
8d	0.5	0.22	0.44	0.085	0.10
5f	0.5	0.37	0.74	0.24	0.245
74	0.5	0.57	1.14	0.45	0.46
7b	0.5	0.96	1.92	0.86	0.88
22a	0.5	0.25	0.50	0.12	0.12
9c	0.5	0.23	0.46	0.095	0.096
15b	0.5	0.175	0.35	0.037	0.032
9c	3.0	1.07	0.36	0.093	0.096
21b	3.0	0.93	0.31	0.060	0.064
15b	3.0	0.74	0.25	0.020	0.032
12c	3.0	0.68	0.23	0.007	0.016

The results using the Bureau of Standards samples are satisfactory and show a relatively small error. The method has been used on routine work and found to be more reliable than the older phosphomolybdate methods when an inexperienced operator is using them. The only serious interference with the method is brought about by large amounts of silicon, as in 4 per cent silicon steels. In such cases, this method will not work, for the formation of yellow silicomolybdic acid vitiates any measurement on the color caused by

small amounts of phosphorus. Excepting such cases, the method appears to be very reliable and useful.

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Determination of Pyrethrin I

In Commercial Insecticides Containing Pyrethrum or Pyrethrum Extract

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PYRETHRUM insecticides consist of pyrethrum powder or mixtures containing it; mineral oil containing pyrethrum extract, an essential oil or perfume, and frequently other substances such as derris extract or organic thiocyanates; or, in the case of plant sprays, essential oils, an emulsifier such as soap, a sulfated alcohol or sulfonated oil, pyrethrum extract, derris extract, and a solvent, usually alcohol, acetone, or water.

The method proposed by Seil (3) has been largely used for the determination of the pyrethrins in pyrethrum powder. A modification of this method has been used for the determination of pyrethrins in mineral oil-pyrethrum sprays. Graham (1), however, reported a loss of pyrethrin I in the preliminary steam distillation in this method when applied to mineral oil sprays, and Wilcoxon (4), working with purified pyrethrum resins, found that the monocarboxylic acid from the pyrethrin I is not completely recovered after the steam distillation for separating it from the dicarboxylic acid, so that a low value for pyrethrin I is obtained. Wilcoxon determined pyrethrin I in pyrethrum flowers by utilizing the reaction between the monocarboxylic acid and Denigès' reagent, by which mercury is reduced, and the determination of the reduced mercury by the iodate method of Jamieson (2). In the author's hands this method has given good results on pyrethrum powders, but unsaturated compounds formed by saponification of perfumes, essential oils, or other substances which may be present in many pyrethrum insecticides interfere with the iodate titration by absorption of iodine.

By modifying Wilcoxon's method so as to remove unsaturated organic compounds, a procedure has been developed for the determination of pyrethrin I in many commercial insecticides. This modification has been used on mineral oil sprays containing pyrethrum extract, essential oils, perfumes, derris extract, and organic thiocyanates, and in the analysis of

plant sprays containing essential oils, derris resins, soaps and other spreaders, tobacco extract, alcohol, or acetone. The method depends on the reduction of Denigès' reagent by the monocarboxylic acid, precipitation of the reduced mercury as calomel, removal of unsaturated organic compounds with acetone and chloroform, and determination of the reduced mercury by titration with iodate solution. The monocarboxylic acid is separated from the dicarboxylic acid by extraction with petroleum ether, in which the free dicarboxylic acid is only slightly soluble. Under the conditions of the determination, the dicarboxylic acid reacts very slowly with Denigès' reagent, so no appreciable error is introduced by the small amount present.

Experimental

In the experimental work an alcoholic extract of pyrethrum flowers was analyzed by Seil's method and by the proposed method. After analysis by the Seil method the titrated solution was acidified and the monocarboxylic acid was extracted with petroleum ether and determined by treatment with Denigès' reagent. These results are given in Table I. Samples were also made up containing the same amount of extract to which were added 5 per cent of pine oil, 4 per cent of oleic acid, and 2 per cent of derris resins. These samples were

TABLE I. PYRETHRUM I IN ALCOHOLIC PYRETHRUM EXTRACTS

	Mercury Reduction Method	Seil Method	Mercury Reduction on Titrated Solution
	%	%	%
Alcoholic pyrethrum extract	0.31 0.32	0.27 0.27	0.21 0.20
Alcoholic extract + pine oil, oleic acid, and derris resins	0.35 0.32	:: ::	:: ::



analyzed by the mercury reduction method. Results are also shown in Table I.

The official control insecticide prepared by the National Association of Insecticide and Disinfectant Manufacturers was used for experimental work on mineral oil-pyrethrum sprays. One per cent of methyl salicylate, one of the most frequent and serious interfering substances, was added to other portions of this spray, which were analyzed by the Seil method and by the mercury reduction method. The titrated solution from the Seil determination was acidified, and the monocarboxylic acid was extracted with petroleum ether and determined by reduction of mercury. Two and one-half per cent of  $\beta$ -butoxy- $\beta'$ -thiocyanodiethyl ether was added to other samples of the spray and these were analyzed by the mercury reduction method. The results are given in Table II.

TABLE II. PYRETHRUM I IN MINERAL OIL-PYRETHRUM EXTRACTS

	Mercury Reduction Method %	Seil Method %	Mercury Re- duction on Ti- trated Solution %
Official control insecticide	0.044	0.042	...
	0.044	0.041	...
Insecticide + 1% methyl salicylate	0.047	...	...
	0.047	...	...
	...	0.050	0.043
	...	0.054	...
Insecticide + 2.5% $\beta$ -butoxy- $\beta'$ -thiocyanodiethyl ether	0.044	...	...
	0.045	...	...

The analyses show that the Seil method and the mercury reduction method give comparable results on mineral oil-pyrethrum sprays which contain no interfering substances. An appreciable amount of the acids titrated in the Seil method, however, is not the monocarboxylic acid. This error is in the opposite direction to that caused by incomplete recovery of the monocarboxylic acid in the steam distillation. These results are similar to those found by Wilcoxon.

In mineral oil sprays containing methyl salicylate, it is difficult to remove all traces of the essential oil by steam distillation; so the result by the Seil method is high.

### Mercury Reduction Method

Measure a sample containing from 20 to 75 mg. of pyrethrin I into a 300-cc. Erlenmeyer flask; add 15 cc. of 0.5 *N* alcoholic sodium hydroxide solution and reflux on a steam bath or electric hot plate for 1 to 1.5 hours. (More sodium hydroxide may be necessary in samples containing large amounts of perfumes or essential oils.) Transfer to a 600-cc. beaker and add sufficient water to make the aqueous layer to 200 cc. Add a few glass beads, or preferably use a boiling tube, and boil the aqueous layer down to 150 cc. Transfer the aqueous layer to a 250-cc. volumetric flask and add 1 gram of Filter-Cel and 10 cc. of a 10 per cent barium chloride solution; make to volume and let settle (in some cases more barium chloride may be needed to obtain a clear solution). Filter off 200 cc., add 5 cc. of sulfuric acid (1 + 4), filter into a 500-cc. separatory funnel, and extract with two 50-cc. portions of petroleum ether. Wash the extracts with several 10-cc. portions of water and filter through a plug of cotton into a clean 250-cc. separatory funnel. Wash the cotton with 5 cc. of petroleum ether. Extract the petroleum ether with 5 cc. of 0.1 *N* sodium hydroxide, shaking vigorously.

Draw off the water layer into a 100-cc. beaker, wash the petroleum ether with 5 cc. of water, and add this to the beaker. Add 10 cc. of Denigès' (U. S. P. XI) reagent to the beaker and let stand 1 hour. Add 20 cc. of acetone to the beaker and precipitate the reduced mercury with 3 cc. of saturated salt solution. Warm to about 60° C., filter through a small filter paper (7 to 9 cm.), and wash with 10 cc. of hot acetone, transferring all the precipitate to the filter paper. Wash with two 10-cc. portions of hot chloroform, and place the filter paper and contents in a 250-cc. glass-stoppered Erlenmeyer flask. Add 30 cc. of concentrated hydrochloric acid and 20 cc. of water to the flask, cool, and add 6 cc. of chloroform or carbon tetrachloride and 1 cc. of iodine monochloride solution [dissolve 10 grams of potassium iodide and 6.44 grams of potassium iodate in 75 cc. of water; add 75 cc. of hydrochloric acid and 5 cc. of chloroform in a glass-stoppered bottle and adjust to a faint iodine color (chloroform) by adding dilute potassium iodide or potassium iodate solution], and titrate

with 0.01 *M* iodate solution (2.14 grams of potassium iodate per liter). Potassium iodate reacts with reduced mercury to form mercuric mercury and iodine. Further addition of iodate in the presence of hydrochloric acid oxidizes the iodine to iodine monochloride.

1.  $5\text{HgCl} + 6\text{HCl} + \text{KIO}_3 = \text{I} + 5\text{HgCl}_2 + \text{KCl} + 3\text{H}_2\text{O}$
2.  $2\text{I}_2 + \text{KIO}_3 + 6\text{HCl} = 5\text{ICl} + \text{KCl} + 3\text{H}_2\text{O}$   
(combining 1 and 2 gives the equation shown by Jamieson)
3.  $4\text{HgCl} + \text{KIO}_3 + 6\text{HCl} = 4\text{HgCl}_2 + \text{ICl} + \text{KCl} + 3\text{H}_2\text{O}$

Addition of iodine monochloride does not change the volume relations between reduced mercury and iodate solution and aids in the titration of small amounts of mercury. The end point is taken when the red color disappears from the chloroform layer. The end point is not permanent; so the titration should be completed rapidly with vigorous shaking after each addition of iodate. One cubic centimeter of the iodate is equivalent to 4.4 mg. of pyrethrin I.

### Summary

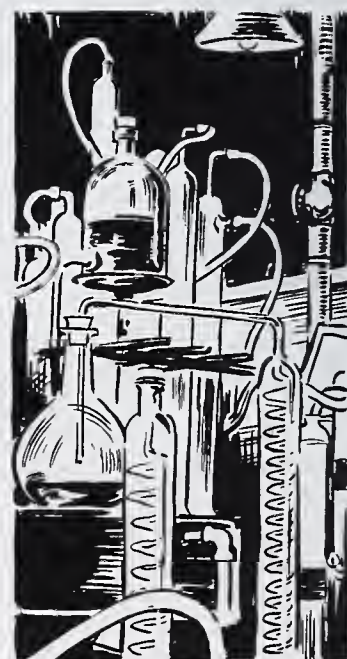
The Seil method for the determination of pyrethrin I in commercial mineral oil-pyrethrum insecticides containing essential oils or perfumes is not satisfactory, as the monocarboxylic acid is not completely recovered by the usual steam distillation and acidic substances other than the carboxylic acid involved, which may be present in the petroleum ether extract of the distillate, will be titrated as this acid. Wilcoxon's method for pyrethrin I is satisfactory for pyrethrum powder only. Essential oils and many other substances, however, interfere with the iodate titration for reduced mercury and cause high results for pyrethrin I.

Wilcoxon's method for the determination of pyrethrin I in pyrethrum powder has been modified so that it can be used in the determination of pyrethrin I in insecticides containing pyrethrum powder or pyrethrum extract, mineral oil, essential oils, perfumes, derris resins, and certain other materials.

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Courtesy, Skinner & Sherman, Inc.



# The Determination of Iron with Mercaptoacetic Acid

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THE reaction between mercaptoacetic acid and iron to give a reddish purple color has been known many years (1, 4), but it was not until 1927 that Lyons (7) applied it to the quantitative determination of this metal. (Mercaptoacetic acid is given a number of names in the literature, such as thioglycolic acid, thioethanoic acid, and thiolacetic acid. Since the reaction occurs in ammoniacal solution, the reagent might more properly be called ammonium mercaptoacetate.) He attributed the color to a complex with ferrous iron and believed that ferric iron is reduced to the ferrous condition by the mercaptoacetic acid, thus accounting for the fact that the color is a function of the total iron present. Cannon and Richardson (3) found that ferric iron in the absence of oxygen gives a red color with this reagent which fades at a rate proportional to the hydrogen-ion concentration over a pH range of 6 to 11, and that ferrous iron gives no color under the same conditions. They concluded that both ferrous and ferric iron form complexes which exist in equilibrium.

Various individuals (2, 6, 8, 10) have adapted the method to the determination of iron in biological materials and foods. Lyons (7) investigated the effect of a number of other ions on the color. Hanzel (5) reported the noninterference of considerable amounts of ortho- or pyrophosphoric acid.

The purpose of the present paper is to describe a quantitative study of the procedure, including the effect of the common ions, made with the more accurate means of color measurement now available.

## Apparatus and Methods

All color measurements were made with a recording General Electric spectrophotometer in the same manner as described previously (9).

A 10 per cent solution, by volume, of mercaptoacetic acid, neutralized with ammonium hydroxide, was used for most of the work. Two milliliters of this reagent and 10 ml. of 3 *M* ammonium hydroxide were used for each determination to make a final volume of 100 ml. Standard solutions of iron were prepared by dissolving weighed amounts of iron wire or ferrous ammonium sulfate in sufficient hydrochloric or sulfuric acid to prevent hydrolysis. A concentration of 0.10 mg. of iron per 100 ml. was used for most of the studies on interference. The solutions of cations and anions were prepared from reagent quality salts. Blank determinations were made to ensure absence of iron.

All amounts of interfering substances mentioned refer to a volume of 100 ml. The limiting amounts for interfering ions were calculated for a permissible error of approximately 3 per cent of iron. This error, for ions which produced only a change in intensity, was calculated by means of Beer's law expressed in the form

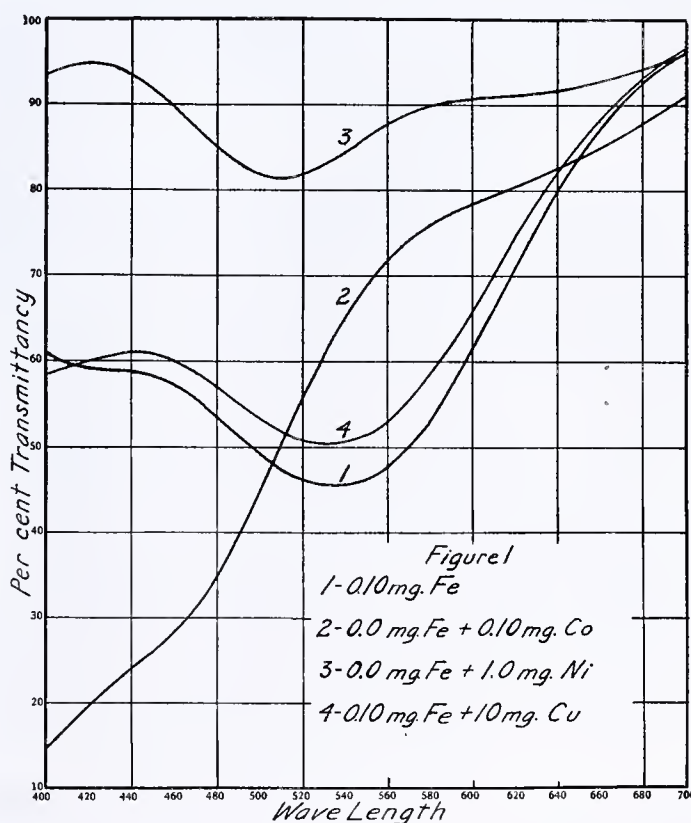
$$T_1 = T_2 \frac{C_1}{C_2}$$

$T_1$  is the transmittancy for an iron concentration of  $C_1$ , at a selected wave length.  $T_2$  is the transmittancy for the same wave length and iron concentration with the interfering ion present.  $C_2$  is the apparent concentration in the presence of

the interfering ion. The spectrophotometric method was supplemented with visual observation for ions which produced color.

## The Color Reaction

A preliminary study of the color reaction showed the intensity of the color to be independent of the form in which the reagent is added and of its concentration, providing an excess is present. Also the concentration of ammonium hydroxide can be varied over a wide range without any noticeable effect. The particular conditions used for this study gave a pH of 10.1 for the solution after dilution to 100 ml.



Various individuals have reported the color to be stable for 30 minutes. According to some observers, the original color intensity, after slight fading has occurred, can be restored by agitation with air. The authors found the color to be relatively stable. Solutions protected from light showed no evidence of fading after 12 hours and were stable for at least 6 hours when exposed to diffuse daylight. These solutions were stored in Erlenmeyer flasks which exposed considerable surface of the liquid to the air. This may account for the greater permanence over that previously reported.

Calculations based on the transmittancy data for a wide range of concentrations showed that the color follows Beer's law very closely, thus allowing the use of a variable depth method of color comparison.

## The Effect of Anions

The mercaptoacetic acid method is remarkably free of interference by the common anions, many of which must be entirely absent for other colorimetric methods. The following

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ions, in concentrations of 500 mg. in 100 ml. of solution, had no effect on the color: fluoride, iodide, nitrate, orthophosphate, sulfate, chlorate, tartrate, oxalate, citrate, acetate, bromide, thiocyanate, sulfite, and chloride. Two hundred fifty milligrams of boron trioxide, present as tetraborate ion, also had no effect.

Pyrophosphate ion, when present in an amount equivalent to 500 mg. of phosphorus pentoxide, decreased the color intensity about 8 per cent. A concentration of 200 mg. gave a decrease of 3 per cent. It is evident that 200 to 300 mg. can be present without serious error. This quantity is smaller than that reported by Hanzel (5) but still well above that usually encountered in an analysis.

Cyanide ion interfered seriously and must be absent.

Nitrite ion, when added to an acidic solution of iron, followed by the reagent and ammonium hydroxide, produced a deep orange color. When this ion was added after the solution was made ammoniacal, no color appeared, indicating that the color was caused by the nitrous acid.

Molybdenum, in the form of molybdate, formed a yellow or orange color at high concentrations. Up to 2 mg. of molybdenum for 0.10 mg. of iron had no appreciable effect.

Tungsten, in the form of tungstate, produced a blue color, but amounts of 2 mg. did not interfere.

Arsenic, in the form of arsenate, had no appreciable effect in amounts up to 50 mg. of the metal.

### The Effect of Cations

Cobalt produced a yellow or red color, depending upon the concentration. Mercaptoacetic acid is nearly as sensitive to it as to iron, as shown by transmittancy curves 1 and 2, Figure 1, for 0.10 mg. of each of these metals. Not more than 0.002 mg. of cobalt can be present for 0.10 mg. of iron without changing the hue and introducing an error of more than 3 per cent.

Nickel reacted with the reagent to give a color similar in hue to that produced by iron but not nearly as intense, as shown in curve 3, Figure 1. With 0.10 mg. of iron 0.01 mg. of nickel can be present.

Copper, on addition to mercaptoacetic acid in hydrochloric acid solution, formed a white precipitate which dissolved to give a nearly colorless solution after an excess of ammonium hydroxide was added. The presence of copper with iron caused a bleaching effect, shown in curve 4, Figure 1, but this was not appreciable for amounts below 1 mg.

Tervalent antimony had no effect in amounts up to 100 mg., but more than this caused a precipitate to form.

Tervalent arsenic bleached the color at concentrations greater than 100 mg. in 100 ml.

Bivalent tin, which ordinarily precipitates with ammonium hydroxide, remained in solution in the presence of the reagent, presumably with the formation of a soluble complex ion. Up to 20 mg. of tin did not affect the accuracy, but larger amounts bleached the color. The use of more reagent partly overcame the bleaching action.

Zinc did not form a colored complex but did react as shown by curve 2, Figure 2. By adding 6 ml. of reagent to provide an excess over that used by the zinc and iron, the full intensity of the color was maintained, as shown in curve 3, Figure 2. If the color intensity were dependent on the exact concentration of the reagent, as in the thiocyanate or ferron methods, the addition of a large excess of reagent could not be used to eliminate interference from metals which react but do not form a color. At least 200 mg. of zinc can be present for 0.10 mg. of iron.

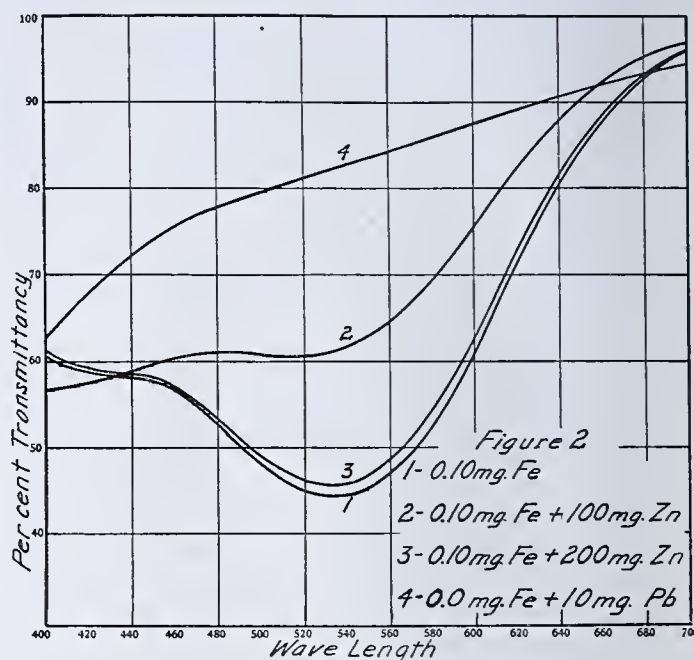
Cadmium behaved in the same manner as zinc. Two hundred milligrams caused no interference when 8 ml. of reagent were used.

Lead formed a yellow or amber color, shown in curve 4,

Figure 2, which limited the amount of lead to 0.10 mg. for 0.10 mg. of iron.

Manganous ion produced an amber color which faded rapidly on standing a few minutes. Stirring caused the color to reappear, followed by fading again. Up to 10 mg. of manganese caused no interference when the solution was allowed to stand undisturbed for a few minutes.

Barium, calcium, and strontium in amounts up to 200 mg. caused no trouble when no ion was present which would produce a precipitate in ammoniacal solution.



Magnesium did not interfere in quantities as high as 250 mg. although it was necessary to add ammonium chloride to prevent the hydroxide from precipitating.

Bismuth, which precipitates with ammonium hydroxide, remained in solution in the presence of the reagent. A yellow color formed which limited the amount to about 0.2 mg. for 0.10 mg. of iron.

Mercurous ion formed a black precipitate but mercuric salts had no effect up to 30 mg.

Uranyl ion produced an intense orange color. More than 0.02 mg. made a color match impossible.

Gold gave an amber color which was not appreciable for amounts below 0.2 mg.

An amber color which was not reproducible or proportional to the concentration was produced by silver. Only about 0.2 mg. can be present with 0.10 mg. of iron.

Aluminum and chromium were precipitated by ammonium hydroxide. Sodium, potassium, and ammonium ions had no effect at low concentrations. Extremely high concentrations of salts caused a slight decrease in the color intensity.

### Discussion

It is evident from the data presented that the mercaptoacetic acid method possesses a number of advantages not found in most other colorimetric methods for total iron. Conformity to Beer's law and independence of the color with respect to the exact reagent concentration and the pH make the method easy and rapid to use. The color, while not extremely stable, does not fade so rapidly that color comparisons are difficult. One set of standards can be used for a number of determinations. At the present time several large manufacturers are using this method for routine analyses.

With respect to interference from anions, the method is much superior to those which are based on reaction with ferric iron. It is almost completely free from interference by



phosphate, pyrophosphate, fluoride, tartrate, citrate, and oxalate ions, all of which exhibit a strong tendency to form stable complexes with ferric iron. For the analysis of materials which contain phosphates, the method is especially to be recommended.

A number of metals interfere, but some of these are seldom found in appreciable amounts with iron. A more serious fault is the use of an alkaline solution, which precipitates many metals.

The limiting amounts of interfering ions are specified for a volume of 100 ml. and an iron content of 0.10 mg. With smaller amounts of iron, the apparent interference will be greater for some metals, thus lowering the amount that can be present without serious interference.

Conclusions

The effect of the common cations and anions on the mercaptoacetic acid method for iron has been studied, as well as

the general conditions affecting such methods. The lack of interference by nearly all anions and the reproducibility and sensitivity of the color reaction make the method superior to various other colorimetric procedures for iron.

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Turbidity in Sugar Products

VI. Generalized Method and Formulas for the Determination of Color and Turbidity in Colored Media

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THE recent work of the writers (3) on the turbidity and color of white sugars has shown that the absolute turbidity, calculated according to Sauer's system (2), is directly proportional, within the limits of error of the method, to the turbidity found by the method of the writers with this type of sugars. This fact suggested a reexamination of the data obtained with raw sugars, where no such proportionality had been observed (5). The writers have therefore calculated the absolute turbidity of the 21 sirup mixtures containing known proportions of color and turbidity (4), by the formula of Sauer:

Absolute turbidity (S) = A f<sub>k</sub>D t (1)

where A is the relative Tyndall beam intensity, measured with the Pulfrich photometer, and equals 0.01 R in the system used by the writers. D is a factor varying with the thickness of the absorption cell, and equals 6.6395 for the 2.455-mm. cells used; t is the absolute turbidity of the standard glass block of the instrument, in this case 0.00282 for the green filter. The factor f<sub>k</sub> is a function of the extinction coefficient (−log T for 1-cm. thickness) of the solution measured.

The relation between f<sub>k</sub> and k has been derived by Sauer from theoretical considerations, and is expressed (1) by the following formula:

f<sub>k</sub> = (kd(√2 - 1) × 2.30259) / (10<sup>-kd</sup> {1 - 10<sup>-kd(√2 - 1)}</sup>) (2)

where d is the depth of layer, in centimeters.

The form of this equation would seem to indicate that f<sub>k</sub> equals 0 when k equals 0. It must be remembered, however, that k is a logarithm; hence log f<sub>k</sub> equals 0 for k equal to 0, and f<sub>k</sub> itself equals 1 under that condition.

A table of f<sub>k</sub> values for varying extinction

coefficients and for varying thickness has been published by Landt and Witte (1). When the logarithms of f<sub>k</sub> are plotted against the extinction coefficient k at constant thickness, a nearly straight line is obtained, starting at f<sub>k</sub> = 0, and k = 0, and satisfying approximately the equation

f<sub>k</sub> = m<sup>k</sup> (3)

where m is a constant showing slight fluctuations.

The values of Sauer's f<sub>k</sub>, at a thickness of 2.455 mm. and corresponding to the extinction coefficients of the 21 mixtures, are shown in Table I, column 5, and the absolute turbidities, S, calculated by Equation 1, in column 6. Three of the mixtures—viz., those highest in turbidity—show absolute turbidities well above unity, which is an impossibility because the intensity of the Tyndall beam cannot be greater

TABLE I. COMPARISON BETWEEN TURBIDITY DATA  
According to Sauer's system and the system of Zerban and Sattler, for mixtures containing known proportions of turbidity and coloring matter.

1	2	3	4	5	6	7	8	9
No.	Composition of Mixtures	N	C	f <sub>k</sub>	S, Based on f <sub>k</sub>	f <sub>k</sub> ' = bc	S, Based on f <sub>k</sub> '	f <sub>k</sub> ' from Sauer's Formula
1	5 U, 0 F, 0 W	0.5155	0.4276	13.288	2.2724	3.367	0.5758	3.259
2	4 U, 1 F, 0 W	0.4378	0.4170	10.450	1.5636	3.268	0.4890	3.166
3	3 U, 2 F, 0 W	0.3051	0.4601	8.205	0.7573	3.692	0.3408	3.563
4	2 U, 3 F, 0 W	0.2147	0.4395	6.063	0.4176	3.482	0.2398	3.370
5	1 U, 4 F, 0 W	0.1179	0.4528	4.826	0.1758	3.616	0.1317	3.493
6	0 U, 5 F, 0 W	0.0287	0.4245	3.497	0.0336	3.341	0.0321	3.219
7	4 U, 0 F, 1 W	0.4175	0.3495	8.245	1.3872	2.764	0.4664	2.629
8	3 U, 1 F, 1 W	0.2932	0.3764	6.323	0.7113	2.911	0.3275	2.831
9	2 U, 2 F, 1 W	0.2105	0.3684	4.935	0.4077	2.846	0.2351	2.770
10	1 U, 3 F, 1 W	0.1259	0.3545	3.768	0.1936	2.737	0.1406	2.666
11	0 U, 4 F, 1 W	0.0264	0.3371	2.733	0.0310	2.603	0.0295	2.541
12	3 U, 0 F, 2 W	0.3200	0.2581	4.924	0.8456	2.081	0.3574	2.044
13	2 U, 1 F, 2 W	0.2086	0.2609	3.657	0.4060	2.098	0.2330	2.060
14	1 U, 2 F, 2 W	0.1161	0.2599	2.828	0.1752	2.092	0.1297	2.054
15	0 U, 3 F, 2 W	0.0303	0.2440	2.138	0.0362	2.001	0.0338	1.966
16	2 U, 0 F, 3 W	0.2224	0.1510	2.808	0.4542	1.535	0.2484	1.521
17	1 U, 1 F, 3 W	0.1154	0.1941	2.355	0.1750	1.734	0.1289	1.713
18	0 U, 2 F, 3 W	0.0151	0.1729	1.684	0.0174	1.635	0.0169	1.615
19	1 U, 0 F, 4 W	0.1035	0.0880	1.700	0.1530	1.284	0.1156	1.277
20	0 U, 1 F, 4 W	0.0115	0.0827	1.299	0.0131	1.267	0.0128	1.258
21	0 U, 0 F, 5 W	0.0036	0.0000	1.000	0.0040	1.000	0.0040	1.000



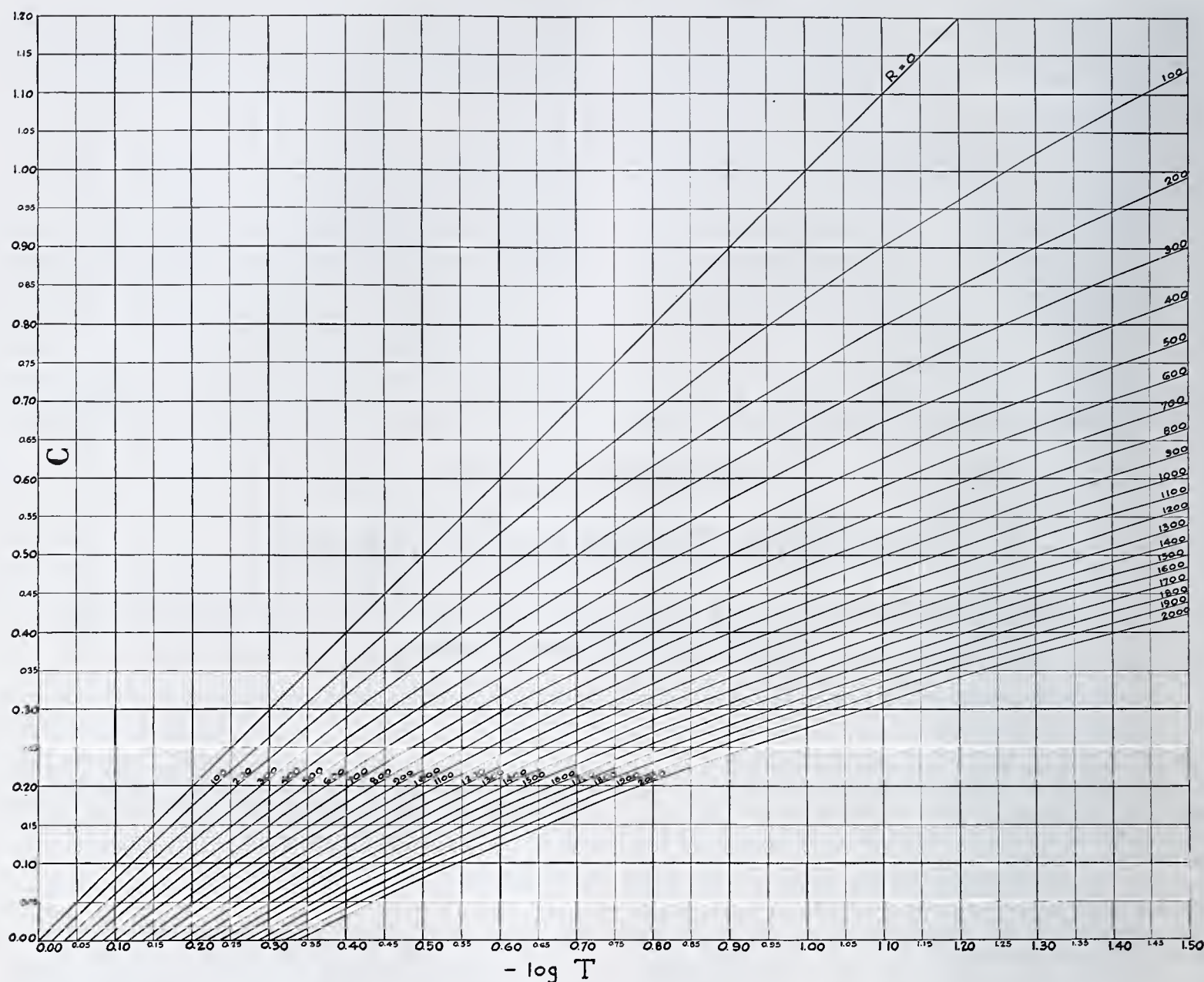


FIGURE 1. CURVES FOR FINDING  $C$  FROM  $-\log T$  AND  $R$ . FULL RANGE FOR WHITE AND RAW SUGARS

than that of the incident light. The relative turbidities of mixtures 1, 7, 12, 16, and 19, which are known to be in the proportion of about 5 : 4 : 3 : 2 : 1, are found to be in the proportion of 14.86 : 9.07 : 5.53 : 2.90 : 1. In other words, the discrepancies between the turbidity present and that found increase rapidly with an increase in known turbidity. This proves conclusively that the correction factors  $f_k$ , if based on  $k$ , are erroneous.

The following considerations will indicate what the values of the correction factors should really be for the 21 mixtures. In the work on white sugars the ratio between the absolute turbidity,  $S$ , and that expressed in terms of  $N$  (as  $-\log T$ , 2.455 mm.), was found to equal 1.117. By substituting 1.117  $N$  for  $S$  in Equation 1, the correction factor, which will be designated by  $f_k'$ , may be calculated for the 21 mixtures:

$$f_k' = \frac{1.117 N}{0.01 R \times 6.6395 \times 0.00282} \quad (4)$$

The values of  $N$ , calculated by the writers' formulas (4), in terms of  $-\log T$  for 2.455-mm. thickness, are shown in Table I, column 3, and those of  $f_k'$  in column 7.

Examination of these  $f_k'$  values disclosed the fact that they are numerically equal to  $b^c$  ( $C$  represents coloring matter) in the formula established by the writers:

$$R = aNb^{-c} \quad (5)$$

or

$$R = \frac{aN}{b^c} \quad (6)$$

where  $C$  is also expressed as  $-\log T$  for 2.455-mm. thickness;  $b$  has been substituted for the symbol  $k$  used originally, to avoid confusion with Sauer's  $k$ .

It is thus clearly shown that the correction factor is a function of the coloring matter alone, and not of  $k$ , which expresses the total absorbency due to coloring matter plus turbidity. The formula of Sauer, Equation 1, and that of the writers are of the same general form:

$$S = 0.01 R \times f_k' \times D \times t \quad (7)$$

$$N = R \times b^c \times 1/a \quad (8)$$

and, since  $f_k'$  equals  $b^c$ , the only difference between the two formulas is in the constants,  $0.01 D \times t$  in one case, and  $1/a$  in the other. This difference is due to the fact that in Sauer's formula the turbidity is expressed as a fraction of the intensity of the incident light, while in that of the writers it is expressed as  $-\log T$  for 2.455-mm. thickness. The ratio between the two constants,  $0.01 D \times t$  divided by  $1/a$ , or  $0.01 D \times t \times a$ , represents the ratio between  $S$  and  $N$ . Substi-



tuting the numerical values of  $D$ ,  $t$ , and  $a$ , we obtain  $0.066395 \times 0.00282 \times 5963.7 = 1.1166$ , which checks the figure found experimentally and used in Equation 4.

If  $f_{k'}$  is now calculated for the 21 mixtures, on the basis of  $C$  (as  $-\log T$ , 1 cm.), instead of  $k$ , by Sauer's formula for  $f_k$ , Equation 2, the figures shown in Table I, column 9, are obtained. These values check closely with  $b^C$  and with the  $f_{k'}$  values calculated from Equation 4.

This result may be interpreted in two ways. Either  $\log f_{k'}$  is really a linear function of  $C$ , as found by the authors' experiments, or else the true relationship between  $f_{k'}$  and  $C$  is correctly expressed by Sauer's formula based on theory. It is logical to accept the latter alternative and to ascribe the strictly linear relationship found experimentally to permissible error. Sauer's formula is thus found to be correct in form, but the correction factor must be based on the color alone.

The original formulas of the writers must then be modified as follows:

By substituting  $f_{k'}$  for  $b^C$  in Equation 8, we obtain

$$N = \frac{Rf_{k'}}{a}$$

(9)

Since  $-\log T = C + N$

(10)

$$C = -\log T - N$$

(11)

Combining Equations 9 and 11 gives

$$C = -\log T - \frac{Rf_{k'}}{a}$$

(12)

This value for  $C$  is now substituted for  $kd$  in Sauer's equation. Since Sauer's  $k$  is now expressed as  $-\log T$  for 1 cm., while  $C$  is  $-\log T$  for 0.2455 cm.,  $C$  must first be divided by 0.2455 to reduce it to 1-cm. thickness, and the quotient must then be multiplied by  $d = 0.2455$  cm. The net result is  $C$  in place of  $kd$ , and the symbol for the correction factor on the basis of  $C$  for 0.2455 cm. is now changed to  $f_C$ . The formula for  $f_C$  thus becomes

$$f_C = \frac{\left\{ -\log T - \left( \frac{Rf_C}{a} \right) \right\} (\sqrt{2} - 1) \times 2.30259}{10 \left[ -\log T - \left( \frac{Rf_C}{a} \right) \right] - \left\{ -\log T - \left( \frac{Rf_C}{a} \right) (\sqrt{2} - 1) \right\}}$$

(13)

There remains some uncertainty about the true value of constant  $a$ , which is derived from the writers' experimental data and is subject to the same sources of error as constant  $b$ . But since there appears to be no theoretical correlation between  $D \times t$  and  $a$ , the value found experimentally will be accepted for the present.

The physical significance of constant  $a$  may be derived from Equation 12. When  $C$  equals 0 and consequently  $f_C$  is equal to unity,  $a$  equals  $R/(-\log T)$ . This relationship makes it possible to check  $a$  experimentally, and also to tell whether coloring matter is present in significant amounts, because in its absence the ratio between  $R$  and  $-\log T$  should not vary.

In order to calculate  $C$  and  $N$  from  $R$  and  $-\log T$ , Equation 13 is solved for varying values of  $C$ , which is the  $-\log T - (Rf_C/a)$  term, and a tabulation of corresponding  $f_C$  values is thus obtained. Substitution of these  $C$  and  $f_C$  values at specified increments of  $R$  in Equation 12 yields a table from which  $C$  may be found for any pair of  $-\log T$  and  $R$  values. Practically,  $C$  is found from curves based on the table, and  $N$  is obtained by subtraction from  $-\log T$ .

A graph covering the entire range of  $C$ ,  $-\log T$ , and  $R$  values of raw sugars is shown in Figure 1. A blueprint of the large working graph, in which increments of 0.1  $C$  and 0.1 ( $-\log T$ ) are made equal to 50 mm., will be gladly sent to anyone expressing a desire for it. From the graph the  $C$  corresponding to given values of  $-\log T$  and  $R$  can be read off directly with close approximation to the third significant figure.

If more exact results are desired, interpolation for  $R$  is carried out by means of Table II, on the basis of the approximate value of  $C$  read from the graph. The use of the table is best explained by an example. A raw sugar sample gave  $-\log T = 0.57807$ , and  $R = 917.1$ , for the green filter. A glance at the graph shows that  $C$  lies between 0.25 and 0.30. The value of  $Rf_C/a$  for 1  $R$ , at  $C = 0.25$ , is 0.0003351; hence that for 917.1  $R$  is  $0.0003551 \times 917.1$ , or 0.30732, which added to 0.25  $C$  gives  $-\log T = 0.55732$ . Similarly, the value of  $Rf_C/a$  for 1  $R$ , at  $C = 0.30$ , is 0.0003847, and that for  $R = 917.1$  is 0.35280, which added to 0.30 gives  $-\log T = 0.65280$ . Then the difference,  $x$ , between the required value of  $C$  and the value 0.25 is found from the following equation:

$$(x - 0.25) : (0.30 - 0.25) =$$

$$(0.57807 - 0.55732) : (0.65280 - 0.55732)$$

The result for  $x$  is 0.0109, which added to 0.25 gives a value of 0.2609 for  $C$ .  $N$  equals  $0.57807 - 0.2609$ , or 0.3172.

The above interpolation assumes linear relationship between  $Rf_C/a$  and  $C$  for the small trajet between 0.25  $C$  and 0.30  $C$ . The curve shows that this is not quite correct. The aberration, however, is so slight that the result obtained is well within the limits of error of the photometric data. If the interpolation is made on the basis of the more exact linear relationship between  $\log Rf_C/a$  and  $C$ , the result for  $C$  is 0.2611.

TABLE II. INTERPOLATION TABLE FOR FINDING  $C$  AND  $f_C$  FROM  $-\log T$  AND  $R$

		$\frac{Rf_C}{a}$ for $R = 1$		$\frac{Rf_C}{a}$ for $R = 1$	
$C$	$f_C$	$C$	$f_C$	$C$	$f_C$
0.0000	1.0000	0.0001677	0.1000	1.3200	0.0002213
0.0010	1.0027	0.0001681	0.1500	1.5160	0.0002542
0.0020	1.0055	0.0001686	0.2000	1.7406	0.0002919
0.0030	1.0083	0.0001691	0.2500	1.9986	0.0003351
0.0040	1.0110	0.0001695	0.3000	2.2941	0.0003847
0.0050	1.0138	0.0001700	0.3500	2.6331	0.0004415
0.0060	1.0166	0.0001705	0.4000	3.0214	0.0005066
0.0070	1.0194	0.0001709	0.4500	3.4664	0.0005813
0.0080	1.0222	0.0001714	0.5000	3.9757	0.0006667
0.0090	1.0250	0.0001719	0.5500	4.5598	0.0007646
0.0100	1.0278	0.0001723	0.6000	5.2281	0.0008767
0.0110	1.0306	0.0001728	0.6500	5.9937	0.0010050
0.0120	1.0335	0.0001733	0.7000	6.8699	0.0011520
0.0130	1.0363	0.0001738	0.7500	7.8727	0.0013201
0.0140	1.0391	0.0001742	0.8000	9.0199	0.0015125
0.0150	1.0420	0.0001747	0.8500	10.3329	0.0017327
0.0160	1.0448	0.0001752	0.9000	11.8342	0.0019844
0.0170	1.0477	0.0001757	0.9500	13.5520	0.0022724
0.0180	1.0506	0.0001762	1.0000	15.5154	0.0026017
0.0190	1.0535	0.0001767	1.0500	17.7609	0.0029782
0.0200	1.0564	0.0001771	1.1000	20.3270	0.0034085
0.0220	1.0622	0.0001781	1.1500	23.2604	0.0039004
0.0240	1.0680	0.0001791	1.2000	26.6117	0.0044623
0.0260	1.0739	0.0001801	1.2500	30.4415	0.0051045
0.0280	1.0798	0.0001811	1.3000	34.8136	0.0058376
0.0300	1.0862	0.0001821	1.3500	39.8110	0.0066756
0.0350	1.1023	0.0001848	1.4000	45.5150	0.0076321
0.0400	1.1175	0.0001874	1.4500	52.0280	0.0087242
0.0450	1.1332	0.0001900	1.5000	59.4610	0.0099706
0.0500	1.1488	0.0001926	1.5500	67.9469	0.0113936
0.0550	1.1647	0.0001953	1.6000	77.6286	0.0130170
0.0600	1.1814	0.0001981	1.6500	88.6764	0.0148696
0.0650	1.1978	0.0002008	1.7000	101.1057	0.0169537
0.0700	1.2146	0.0002037	1.7500	115.6513	0.0193928
0.0750	1.2316	0.0002065	1.8000	132.0390	0.0221408
0.0800	1.2491	0.0002095	1.8500	150.7322	0.0252753
0.0850	1.2661	0.0002123	1.9000	172.0380	0.0288479
0.0900	1.2838	0.0002153	1.9500	196.3277	0.0329209
0.0950	1.3017	0.0002183	2.0000	224.0030	0.0375616



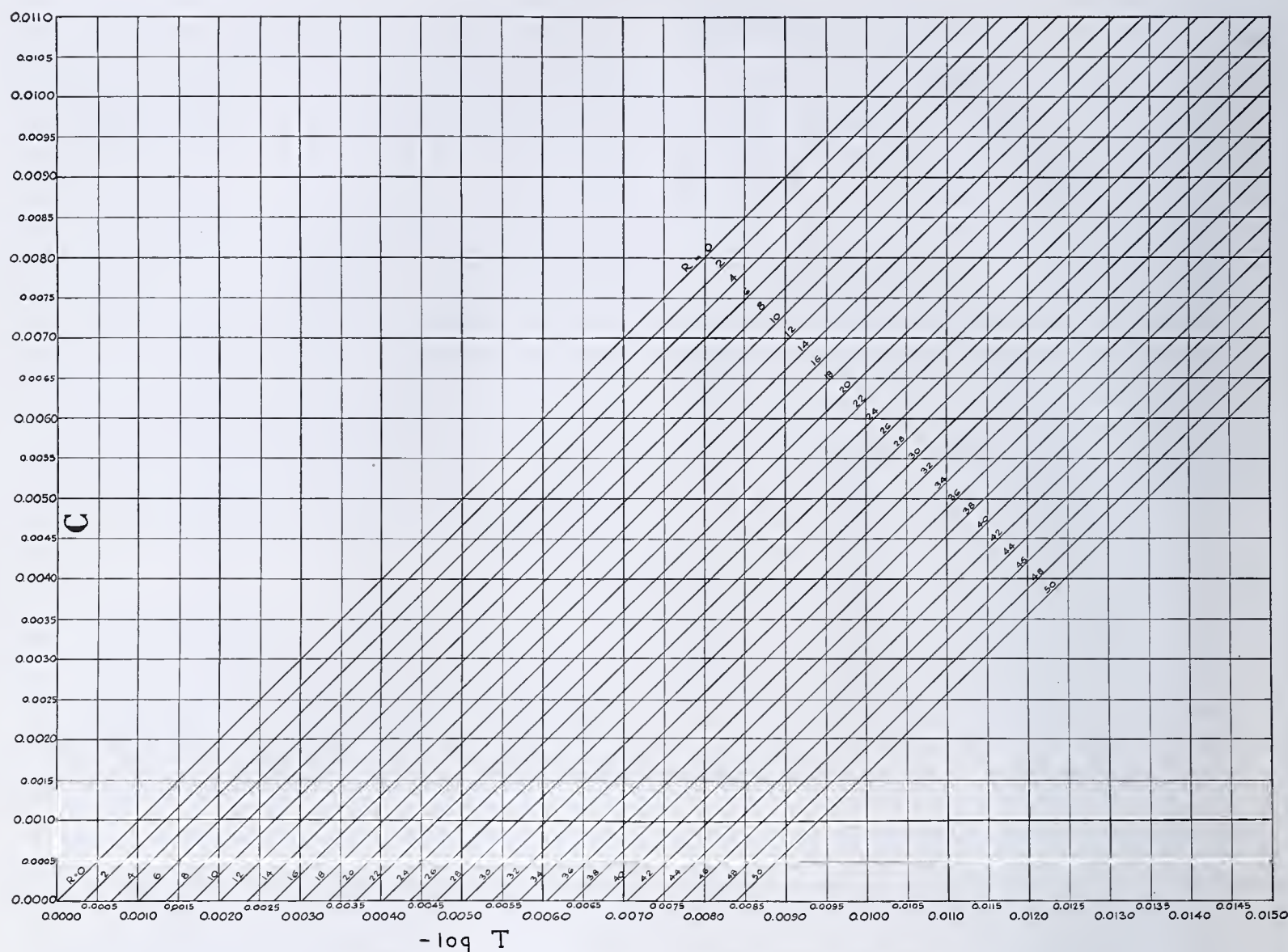


FIGURE 2. ENLARGED GRAPH OF LOWER PORTION OF FIGURE 1

The absolute turbidity can also be readily calculated by means of Table II. By interpolation of column 2 in this table, the  $f_c$  for  $C(kd)$  equal to 0.2609 is found to be 2.0630. By substituting this figure in Sauer's Equation 1, with  $A (0.01 R) = 9.171$ ,  $D = 6.6395$ , and  $t = 0.00282$ , we find the absolute turbidity to equal 0.3542. The ratio between this and the  $N$  found previously (0.3172) is again 1.117.

TABLE III. COMPARISON OF CALCULATED AND FOUND VALUES OF  $C$ ,  $N$ ,  $T$ , AND  $R$  FOR 21 SIRUP MIXTURES

No.	$C$ Calcd.	$C$ Found	$N$ Calcd.	$N$ Found	$T$ Calcd.	$T$ Found	$R$ Calcd.	$R$ Found
1	0.4355	0.4368	0.5200	0.5163	11.08	11.40	933	916
2	0.4355	0.4384	0.4187	0.4164	13.99	13.97	751	738
3	0.4355	0.4465	0.3173	0.3187	17.67	17.17	569	559
4	0.4355	0.4392	0.2160	0.2150	22.31	22.17	387	381
5	0.4355	0.4525	0.1147	0.1182	28.17	26.87	206	202
6	0.4355	0.4399	0.0133	0.0133	35.58	35.22	23.9	23.5
7	0.3484	0.3687	0.4168	0.3983	17.17	17.10	906	857
8	0.3484	0.3663	0.3193	0.3023	21.49	21.40	688	657
9	0.3484	0.3671	0.2218	0.2118	26.90	26.37	482	457
10	0.3484	0.3629	0.1244	0.1175	33.67	33.08	267	257
11	0.3484	0.3339	0.0268	0.0296	42.15	43.30	67.3	69.9
12	0.2613	0.2644	0.3134	0.3137	26.56	26.42	907	898
13	0.2613	0.2580	0.2178	0.2115	33.18	33.92	612	624
14	0.2613	0.2552	0.1221	0.1208	41.36	42.07	349	350
15	0.2613	0.2490	0.0264	0.0253	51.56	53.17	73.2	75.7
16	0.1742	0.1543	0.2100	0.2191	41.29	42.33	806	851
17	0.1742	0.1843	0.1102	0.1252	51.95	49.03	461	447
18	0.1742	0.1764	0.0125	0.0116	65.06	64.87	42.7	42.1
19	0.0871	0.0883	0.1070	0.1032	63.96	64.35	483	481
20	0.0871	0.0828	0.0121	0.0114	79.58	80.50	53.4	54.1
21	0.0000	0.0000	0.0036	0.0036	99.17	100.00	21.5	21.6

The new method of calculation has been applied to the 21 sirup mixtures mentioned before (Table I), and the calculated values of  $C$ ,  $N$ ,  $T$ , and  $R$  are compared with those found experimentally in Table III.

The agreement between found and calculated values is satisfactory if it be considered that thorough mixing of the heavy constituent sirups was a difficult matter because agitation tends to disturb the colloid equilibrium.

For products which are low in both color and turbidity, the graph shown in Figure 2 is used. If the scale is such that  $C$  and  $-\log T$  are plotted at 50 mm. = 0.001 unit, it is possible to read  $C$  and  $-\log T$  values accurately to the fourth decimal place. A blueprint of this graph is also available. In this range linear interpolation is accurate. For such computational purposes Table II is used in exactly the same way as in the previous case.

$C$  and  $N$  have been calculated in this manner for the refined sugars previously examined (3). As was to be expected, the results obtained checked with those calculated by the original formulas of the writers within one unit of the fourth decimal place.

With this type of sugars, representing a practically colorless medium, it is permissible to calculate the absolute turbidity directly by the use of Sauer's formula and the correction factor based on the  $-\log T$  of the turbid solution rather than on  $C$ , and to find  $N$ , expressed as  $-\log T$ , by dividing by 1.117.  $C$  then equals  $-\log T - N$ .

Conversion of  $-\log T$  and of  $R$  values determined at one thickness into the corresponding figures at another thickness,



or of  $-\log T$  into  $-\log t$  values, may be made as explained in the preceding paper of this series (3).

### Summary

A reexamination of previous data has shown that the correction factor for absorption, in Sauer's formula for the calculation of absolute turbidity, must be based on the concentration of coloring matter alone, and not on the total light-absorbing material including the turbidity. In all other respects Sauer's formula is of the same form as that developed by the writers, and if the correction factor, derived from theory, is based on the coloring matter only, its numerical value checks that of the term  $k^c$  in the original formula of the writers, which was based on purely experimental evidence. Sauer's principle has therefore been accepted as a basis for calculating the correction factor from only the concentration of

the coloring matter, and the writer's formula has been modified by substituting the new correction factor for their  $k^c$  term. It is thus possible to use the same correction factor for calculating either the absolute turbidity according to the modified Sauer formula, or the coloring matter and turbidity, expressed as  $-\log T$ , by the revised formula of the writers.

The new formulas have been checked against the experimental data, and satisfactory agreement has been found.

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# Determination of Iron in Biological Materials

## The Use of *o*-Phenanthroline

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FOR several years *o*-phenanthroline has been used in the Research Laboratory of the Children's Fund of Michigan as a satisfactory reagent for the determination of iron in foods, feces, blood stroma (1), and other types of biological materials. Since numerous requests have been made for the details of the procedure followed, it seems desirable to record the method in full.

The small amount of iron present in some biological materials precludes the use of the classical gravimetric or titration methods; various colored compounds of iron have therefore been adapted to colorimetric determination. Several of these procedures have been investigated by the authors, but have not been found satisfactory. The presence of large amounts of phosphate in biological materials, especially certain foods and feces, interferes with methods involving the ferric ion, and has necessitated the use of tedious modifications to avoid this interference. For this reason attention has been turned to the color reactions of ferrous iron, which does not form a stable complex with pyrophosphate.

The colored complex formed by ferrous iron with *o*-phenanthroline, which was originally observed by Blau (2), has been used for the determination of iron in various types of materials. The orange-red color is quantitatively proportional to the concentration of iron within the pH range 2.5 to 8.0, and has been used therefore in both titration (7), and colorimetric (6) methods. The colored complexes formed by iron with  $\alpha, \alpha'$ -dipyridyl (2, 4) and *o*-phenanthroline have much the same characteristics, with the advantage that the latter reagent is less expensive and more readily available. (*o*-Phenanthroline may be purchased from the G. Frederick Smith Chemical Company, Columbus, Ohio. The current price is about \$1.75 per gram.)

The method described herein was originally devised for use in the colorimeter, but has since been adapted to the Cenco-Sheard-Standard photometer (5). The latter instrument possesses certain advantages over the colorimeter, since the use of light filters widens the range of accuracy. The relation of density of color to the concentration of iron is determined

at the outset of the experiment (Figure 1) which obviates making up a standard simultaneously with the unknown.

### Reagents

**STANDARD IRON SOLUTION.** Dissolve 1 gram of electrolytic iron in 10 per cent sulfuric acid and dilute to 1 liter. Dilute 1 to 10 for use; 1 cc. of diluted standard corresponds to 0.1 mg. of iron.

**HYDROQUINONE.** Dissolve 1 gram of hydroquinone in 100 cc. of sodium acetate-acetic acid buffer solution with a pH of 4.5 (3). Keep the solution in the refrigerator and discard as soon as any color develops.

**SODIUM ACETATE.** 0.2 M, M, and 2 M are convenient concentrations to have available.

***o*-PHENANTHROLINE.** Dissolve 0.5 gram of *o*-phenanthroline monohydrate in 100 cc. of distilled water, and warm to effect solution.

### Procedure

The material to be analyzed (foods and feces dried at 60° to 80° C. were used) is ashed overnight in an electric muffle furnace at 450° to 500° C. The ash is dissolved in the smallest possible amount of dilute hydrochloric acid (1 to 3) and the solution is filtered into a 100-cc. volumetric flask; if the first ashing is incomplete, the paper and residue are reashed, after thorough washing with distilled water, and the ash is dissolved as before and filtered into the same flask. The solution is then made to volume, and an aliquot selected for analysis which will fall within the range of accuracy of the colorimeter or the photometer—i. e., 0.2 to 0.5 mg. or 0.01 to 0.70 mg. of iron, respectively.

Similar aliquots of the above unknown solution are measured into both a 25-cc. volumetric flask and a test tube, and 2 M sodium acetate solution is added from a buret to the test tube until the color corresponding to pH 3.5 is reached, using 5 drops of La Motte indicator bromophenol blue. The unknown solution in the 25-cc. volumetric flask is adjusted to pH 3.5, using the same amount of 2 M sodium acetate, followed by the addition of 1 cc. of 1 per cent hydroquinone solution and 1 cc. of *o*-phenanthroline solution. After thorough mixing, the solutions are allowed to stand for 1 hour to assure complete conversion of the iron to the ferrous *o*-phenanthroline complex, and then made to volume and read in either the colorimeter or the photometer.

If the colorimeter is to be used, a series of standards containing from 0.2 to 0.5 mg. of iron is prepared simultaneously with the unknown. Since the color becomes yellow with dilution, it is not feasible to read lower concentrations in the colorimeter. Ac-



curate results are rarely obtained if the unknown varies from the standard by more than 25 per cent; this confirms the observation of other investigators (6).

The procedure for the determination of iron recorded herein differs from that of Saywell and Cunningham (6) in several respects. The large quantity of calcium and phosphorus present in metabolic materials necessitates a concentration of acid sufficient to prevent the precipitation of calcium phosphate, which carries down most of the iron as ferric phosphate. Since the ferrous *o*-phenanthroline complex is not stable in the presence of strong acid, the pH range 3.0 to 4.0 was selected; this acidity permits maximum color development, yet prevents any precipitation. A solution of hydroquinone in a sodium acetate-acetic acid buffer of pH 4.5 has been used effectively to reduce the iron to the ferrous state. Sodium hydrosulfite was also tried as a reducing agent, but was abandoned because it occasionally caused the solutions to become turbid. Since accurate measurement of the hydroquinone solution can be made, and equal quantities used for standard or unknown, traces of iron in the reagent do not cause appreciable error.

Results

The solutions may be read with equal accuracy within the concentration range 0.2 to 0.5 mg. of iron for the colorimeter, and 0.01 to 0.07 mg. for the photometer. The two instruments were used interchangeably in obtaining the results presented in Tables I and II.

The smooth curves shown in Figure 1 were obtained by measuring the color developed by a series of standards in the photometer. Curve A is obtained from the concentration range 0.01 to 0.16 mg. of iron, using a blue filter, when the solutions are read against a solution of the reagents in sodium acetate-acetic acid buffer pH 4.5 set at 100. The effect of traces of iron present in the reagents as impurity is eliminated by using them as the standard instead of distilled water. Curve B is obtained in the same manner for the concentrations 0.1 to 0.7 mg. of iron, using a green filter.

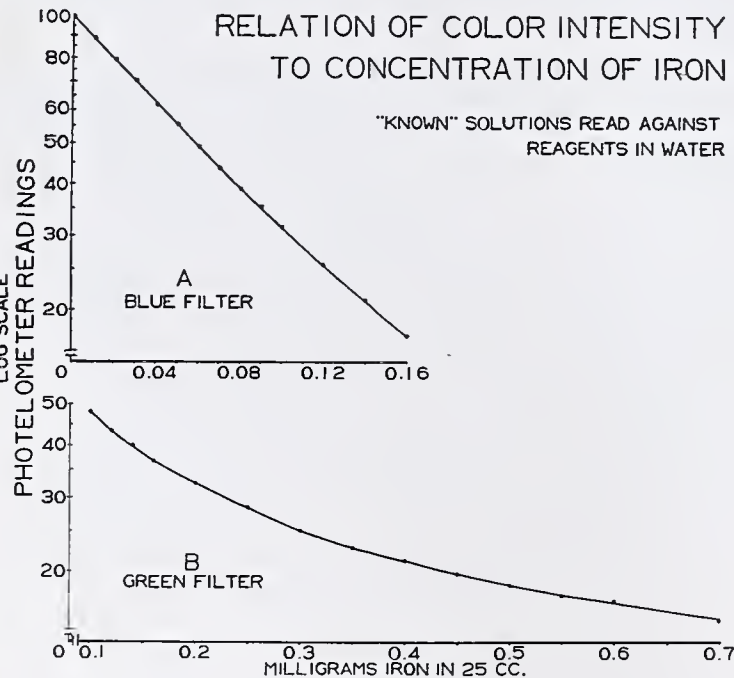


FIGURE 1

Table I shows the recovery of known amounts of iron added to ash solutions. In order to check the accuracy of the dry-ashing method, in some cases the iron was added to the food before ashing. The recoveries are for the most part within the accuracy assigned to colorimetric methods, and dry ashing gives satisfactory results.

TABLE I. RECOVERY OF IRON ADDED TO FOODS BEFORE AND AFTER ASHING

Sample	Determined Mg.	In ash <sup>a</sup> Mg.	Iron		
			Recovered Mg.	Added Mg.	Recovered %
1	0.335	0.234	0.101	0.100	101.0
2	0.250	0.165	0.085	0.0862	98.6
3	0.300	0.165	0.135	0.135	100.0
4	0.435	0.236	0.199	0.200	99.5
5	0.296	0.194	0.102	0.100	102.0
6	0.333	0.194	0.139	0.135	103.0
7	0.284	0.199	0.085	0.0862	98.6
8	0.330	0.199	0.131	0.135	97.0
9	0.374	0.167	0.207	0.200	103.5
10	0.370	0.199	0.171	0.172	99.4
11	0.254	0.167	0.087	0.862	100.9
12	0.339	0.167	0.172	0.172	100.0
13	0.293	0.196	0.097	0.100	97.0
14	0.293	0.196	0.097	0.100	97.0
15	0.390	0.196	0.194	0.200	97.0
16	0.400	0.196	0.204	0.200	102.0
17	0.495	0.196	0.299	0.300	100.0
18	0.250	0.098	0.152	0.150	101.3
19	0.305	0.098	0.207	0.200	103.5
20	0.296	0.098	0.198	0.200	99.0
21	0.350	0.098	0.252	0.250	100.8
22	0.344	0.098	0.246	0.250	98.4

<sup>a</sup> Ashes analyzed separately by the same method.  
Samples 1 to 12: iron was added to ash solution.  
Samples 13 to 22: iron was added to food before ashing.

Since the principal difficulty encountered in colorimetric methods for iron in biological materials especially has been the interference of pyrophosphate, this action was investigated by adding amounts of sodium pyrophosphate representing from 10 to 50 mg. of phosphorus to standard iron solutions. The color was developed in the usual manner, and, after standing from 10 minutes to 24 hours, was read against iron standards containing no pyrophosphate. The results shown in Table II indicate that if the determinations are allowed to stand 30 minutes, the error caused by fairly large amounts of pyrophosphate is within normal limits.

TABLE II. IRON<sup>a</sup> RECOVERED IN PRESENCE OF VARYING AMOUNTS OF PHOSPHORUS

Time of Standing	Phosphorus Added				
	10 mg.	20 mg.	30 mg.	40 mg.	50 mg.
	Iron Recovered				
	Mg.	Mg.	Mg.	Mg.	Mg.
10 min.	0.202	0.199	0.189	0.163	0.161
30 min.	0.200	0.199	0.199	0.196	0.192
1 hour	0.200	0.199	0.199	0.205	0.196
3 hours	0.202	0.198	0.202	0.196	0.195
24 hours	0.201	0.196	0.200	0.200	0.195

<sup>a</sup> All samples contained 0.2 mg. of iron.

The influence of some of the elements which occur in traces in biological materials was investigated. Two milligrams each of lead, zinc, aluminum, mercury, arsenic, fluorine, and iodine, 0.6 mg. of tin, and 0.2 mg. of copper were added to standard iron solutions, and the iron was determined in the usual manner. Since copper reacts with *o*-phenanthroline in amounts over 0.2 mg. and tin precipitates at a pH of 3.5 if more than 0.6 mg. is present, quantities which rarely occur in biological materials, smaller concentrations of these elements were used. No interference was observed.

Preliminary experiments have shown that *o*-phenanthroline may be used for the determination of available iron in foods in much the same manner as  $\alpha,\alpha'$ -dipyridyl (4); it does not form the colored complex when added to purified hematin.

Summary

*o*-Phenanthroline has been used in the quantitative determination of iron in biological materials such as foods, feces, and blood. In the photometer 0.01 to 0.70 mg. of iron can be determined with an accuracy of 3 per cent; the colorimeter can be used with equal accuracy for quantities from 0.2 to 0.5 mg. of iron.

The method is free from interference by pyrophosphate if



sufficient time is permitted for complete conversion of the iron to the ferrous *o*-phenanthroline complex.

None of the elements found in traces in biological materials except copper in amounts over 0.2 mg. and tin in amounts over 0.6 mg. interferes with the determination of iron by this method.

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# Determination of Air and Carbon Dioxide in Beer

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IN VIEW of the relation of air content to beer stability, the determination of the amount of air present in packaged beer has, in recent years, assumed an importance at least equal to that of the determination of carbon dioxide. Such methods for determining air as those of Murray (5), Helm and Richardt (4), and Siegfried (6), while no doubt giving accurate results, are cumbersome and unwieldy.

The chief attribute of the pressure method for determining carbon dioxide, which has been in use for many years in the carbonated beverage industry, is its convenience. In view of the importance attached to air determination, any modification of the pressure method which results in the determination of both air and carbon dioxide at the same time upon the same package in a satisfactorily accurate manner deserves consideration.

In a previous paper (2), the authors worked out a precise chemical method for determining carbon dioxide in bottled beer and carbonated beverages, based on the use of the whole bottle as a sample, a foam suppressant, and an evolution regulating material. Complete liberation of gas was obtained by boiling, the liberated gas being absorbed in alkali and the alkali then being differentially titrated. This method was adopted as tentative by the Association of Official Agricultural Chemists (1).

In the same paper, advantage was taken of the availability of this precise chemical method to study and evaluate the errors inherent in the customary pressure methods for determining carbon dioxide. The authors were able to establish that, if the influence of the variable amounts of air present during the pressure reading is taken into account, accurate carbon dioxide results may be obtained by the pressure method, and that solubility of carbon dioxide in beer, under varying temperature and pressure conditions, can be satisfactorily predicted on the basis of published Henry's law constants for carbon dioxide, assuming that the small amount of alcohol does not affect the total solvent properties of the combined alcohol and water in beer, and that extract has no other effect on solubility than as an inert diluent.

Thus, there was made available an accurate, simple, and convenient pressure procedure once the equipment is at hand. Results presented in the previous paper, as well as experience with the test in the authors' laboratories since that time, amply justify the conclusion that, for most purposes the pressure method, correcting for air and using solubility of carbon dioxide in beer as a basis, yields satisfactory, accurate, and reproducible data for carbon dioxide. The paper (2) outlined

the pressure method and supplied the principles for carrying out the calculations, but did not give in detail the actual method for making the air determination.

Experience with this method has indicated that more accurate results are obtained when all pressure determinations are carried out at 25° C. rather than at much lower temperatures. At this temperature, which is generally easy to maintain, the pressure reading is high, minimizing any gage errors; the air is readily evolved from the beer; and the selection of a single temperature reduces any errors due to differing solubility-temperature coefficients or deviations from gas laws which might enter into the results when determinations are carried out, sometimes at one temperature and sometimes at another. For example, with the much lower pressures prevailing at temperatures close to cellar temperatures in the brewery, a given amount of air will naturally exert, proportionately, a greater effect on the total pressure; in fact, evidence has accumulated that, for the same samples, slightly higher carbon dioxide results are to be expected if the pressures are measured at these lower temperatures.

The authors have also adopted, based on considerable experience with a large number of samples, a revised value for  $\alpha$  (per cent of carbon dioxide per pound pressure) at 25° C.—namely, 0.00965 instead of 0.0095 (3)—embodying an adjustment for such errors as are always involved in assuming an "average beer," and correcting for experimental errors on routine samples. The value has been found to give results which are quite as satisfactory as the precise chemical methods.

In the present paper, details are given for determining both "air" and carbon dioxide by the pressure method. The results of special experiments are also presented, carried out to determine the extent to which the procedure is capable of recovering all the air present in the package. While there is no need, either from the standpoint of controlling air content or as regards the accuracy of the carbon dioxide results, to ensure 100 per cent recovery of the free and dissolved air present, these experiments indicate substantially complete recovery beyond amounts which might be anticipated on the basis of solubility.

Another important factor having a bearing on the accuracy of carbon dioxide results by the pressure method, which has heretofore not been touched upon, is the mechanical difficulties and errors inherent in the usual type of pressure gage. The usual gage, based on mechanical spring action, is frequently found to lag and stick and give erratic results after some use. In view of the frequency with which this occurs,



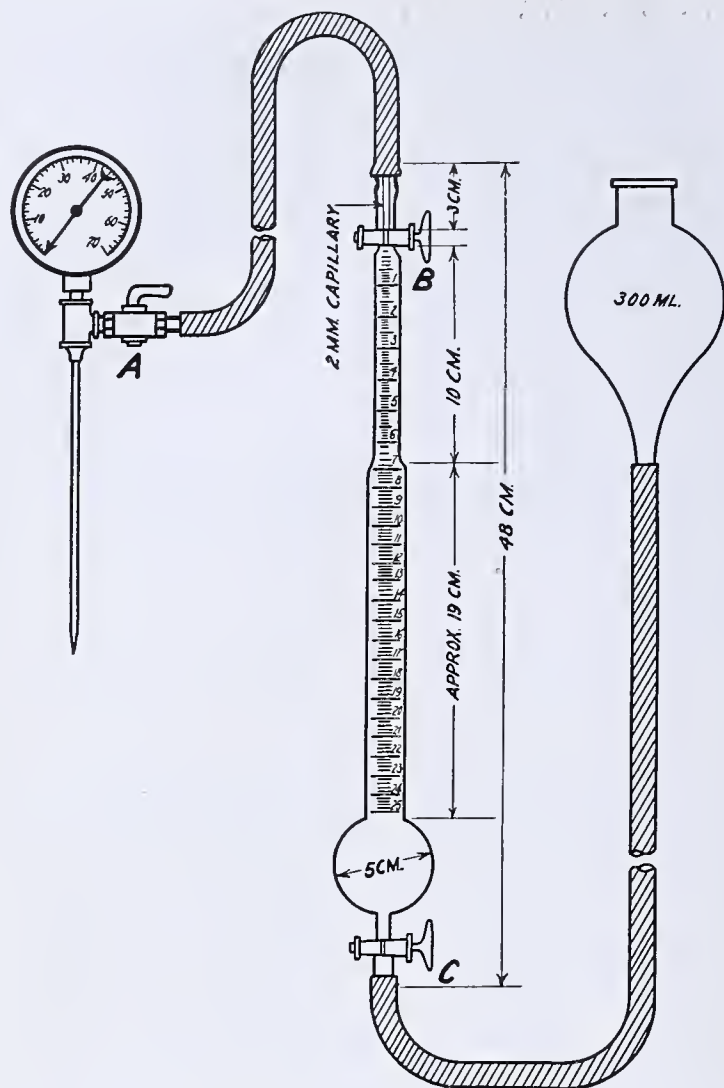


FIGURE 1. ABSORPTION BURET

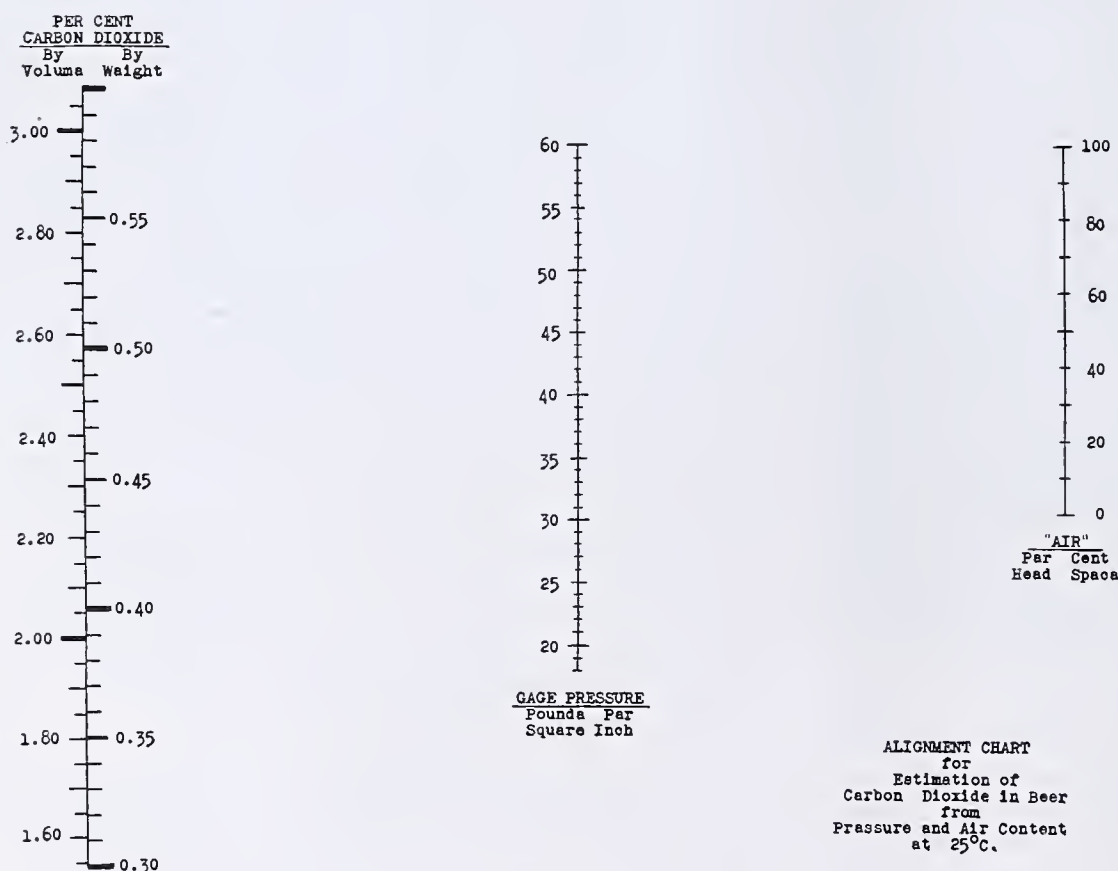
FIGURE 2<sup>1</sup>

Chart copyrighted.

a method was developed for regular calibration of the gages used, based on comparison with a specially constructed mercury manometer. The details of this calibration procedure are also presented.

### Method

**PIERCING APPARATUS FOR BOTTLES.** This consists of a gas-tight packing box and fastening for adjustment over the crown and a hollow spike connected to an accurate pressure gage and outlet valve. A suitable apparatus may be obtained from the C. J. Tagliabue Manufacturing Co., the Liquid Carbonic Corp., the Bishop & Babcock Manufacturing Co., etc.

**PIERCING APPARATUS FOR CANS.** This consists of a metal frame in which the can is placed. The top, which is pressed or screwed down and locked over the can top, contains a hollow spike surrounded by a compressible rubber sealing plug. The hollow spike leads to an accurate pressure gage and an outlet valve.

One apparatus, adjustable for use for bottles and cans, may be employed.

**ABSORPTION BULB.** The bulb consists of a graduated tube (0 to 6 ml. graduated in 0.1-ml. divisions and 6 to 25 ml. graduated in 0.2-ml. divisions) having a bulb, and closed at each end by stopcocks. The upper end is connected by rubber tubing to the outlet valve of the piercing apparatus and the lower end is connected by a length of rubber tubing to a leveling bulb.

**ALKALI SOLUTION.** A 15 per cent solution of sodium hydroxide is used.

**DETERMINATION.** If the sample is in a bottle, make a scratch mark at the beer level. If the sample is in a can, weigh the can with the contents. Submerge the beer in a water bath at 25°C. long enough to bring the temperature of the beer to 25°C. Connect the piercing apparatus to the bottle or can. Fill the absorption bulb with 15 per cent sodium hydroxide solution and allow the solution to run up to stopcock B. Fill the upper capillary of the absorption bulb with hexyl alcohol and the remainder of the system between B and tip of spike with water in order to displace any air. With outlet valve A closed, drive the spike through the crown or can top and thoroughly shake and tap the bottle or can. Make pressure reading on the gage. Again shake and take pressure readings. Use the pressure reading which shows no change in consecutive readings.

Open stopcocks B and C of the absorption bulb and then outlet valve A. Allow the gas, together with foam, to flow over into the absorption bulb. Swirl contents of the bulb to permit absorption of carbon dioxide. When one-half to three-fourths of the alkali solution in the absorption bulb has been displaced, shut off all stopcocks and shake absorption bulb to permit absorption of carbon dioxide. Set the bulb in a vertical position, open bottom stopcock C, and allow alkali to flow back into the bulb. Open stopcocks B and A and repeat the above operation, tapping the bottle or can to accelerate evolution of carbon dioxide. Close upper stopcocks A and B and shake thoroughly to absorb last traces of carbon dioxide. Bring leveling bulb to a position so that the levels of the solution in the leveling bulb and buret are the same and read unabsorbed gas, which is reported as "air." The operation is repeated until consecutive readings as to "air" are the same.

Disconnect bottle or can and determine head space volume as follows:

If the sample is a bottle, fill with water to the top and pour off into a graduated cylinder to scratch mark. The number of milliliters of water thus poured off represents head space in milliliters.

If the sample is a can weigh empty can after pouring out all remaining beer. Difference represents weight of beer which, divided by the specific gravity of the beer,

will give volume of beer in milliliters. Fill empty can with water and weigh. Weight of water in grams is also volume in milliliters, so that the difference between volume of water and volume of beer represents head space in milliliters.

Calculate carbon dioxide by weight by the following formula:

% CO<sub>2</sub> = [ P - (  $\frac{\text{ml. of air}}{\text{ml. of head space}} \times 14.7$  ) ] × 0.00965

P = absolute pressure in pounds per square inch<sup>1</sup> at 25° C. = (ordinary gage pressure + 14.7)<sup>2</sup>

A few typical results are given in Table I.

TABLE I. CARBON DIOXIDE RESULTS ON CONSECUTIVE BOTTLES FROM SAME BOTTLING

Sample	Absolute Pressure at 25° C. Lb./sq. in.	Air, % of Head Space, Ml.	Pressure Correction Lb./sq. in.	CO <sub>2</sub> %
1	49.5	0.7	3	0.474
	50.5	0.8	4	0.482
	51.5	1.9	9	0.484
	52.0	3.8	16	0.479
	52.5	4.2	17.5	0.482
	53.5	6.2	24.5	0.482
2	53	7.3	43	0.451
	54	8.1	48	0.453
	54	9.0	50	0.450
	54	8.2	48	0.453
3	46	5.5	32	0.398
	45	3.6	24	0.401
	45	4.0	25	0.398
	45	3.6	20	0.406
4	45.5	2.1	35	0.389
	48	5.1	51	0.391
	49	4.6	66	0.379
	50	6.4	71	0.382
	50	6.2	69	0.385

Carbon dioxide results for beer need not be reported beyond the second decimal.

In carrying out the pressure-air procedure at 25° C., an alignment chart has been prepared for calculating the corrected carbon dioxide percentage from the gage reading and air result (Figure 2). To use this chart, merely place a straight edge on the determined value of "per cent air in head space" on the right-hand vertical line. Adjust the straight edge so that it also intersects the determined "gage pressure" on the center vertical line. The corrected carbon dioxide value is then read off at the point where the straight edge intersects the left vertical line.

Calibration of Gages

The following procedure was devised for the purpose of calibrating gages, and is used daily in connection with routine tests:

The apparatus consists of a calibrated, isobaric, capillary mercury manometer having a three-way stopcock and means for connecting a tank of carbon dioxide and the gage under test. Figure 3 illustrates the apparatus. The capillary is about 1 mm. in diameter and contains a bulb (of about 50-cc. capacity) which acts as a mercury reservoir and is filled with mercury to the level of the capillary tube as shown.

The capillary, V, is about 45 to 50 cm. (18 to 20 inches) long and the exact volume of the interior is determined as follows: The capillary from line A to stopcock 1 is graduated by divi-

sional marks about 1 cm. apart. Fill the capillary tube with mercury from mark A to the open end, and place in a vertical position. Adjust the mercury level exactly to mark A. The weight of the portions of mercury between each centimeter divisional mark is determined (as in calibrating a buret, except that the weight of the mercury between the last divisional mark and stopcock 1 is also determined). Dividing the weights of mercury by the specific gravity of the mercury at the temperature employed gives the volumes of the capillary bore under the divisions of length V. Adding together the divisional volumes gives the total volume from the inside of stopcock 1 to line A.

Boyle's law states that, at constant temperature, the volume of a gas is inversely proportional to the pressure. For the range of pressures in the simple case at hand, this law may be expressed as follows:

V<sub>1</sub>P<sub>1</sub> = V<sub>2</sub>P<sub>2</sub> = constant

where V<sub>1</sub> = the total volume of tube V above  
P<sub>1</sub> = absolute atmospheric pressure  
P<sub>2</sub> = absolute known pressure applied during testing of gage  
V<sub>2</sub> = compressed volume of gas when pressure P<sub>2</sub> is applied

The absolute pressure is the ordinary gage pressure plus atmospheric pressure. Using Boyle's law and the capillary volume as determined above, the manometer tube is calibrated in pressure readings as follows:

Place the manometer tube in the horizontal position shown in Figure 3. With stopcock 1 open, bring the mercury to line A and close stopcock 1. The air now contained in the space between the mercury and the stopcock has the volume V<sub>1</sub> under atmospheric pressure P<sub>1</sub>. For the sake of simplicity and illustration, we will assume that V<sub>1</sub> = 1 ml. and P<sub>1</sub> = 14.7 pounds per square inch. In order to determine how far the mercury will progress in the tube if a pressure of 5 pounds is applied, we calculate the volume of the enclosed air in V under this pressure (5 pounds per square inch on gage = 14.7 + 5 = 19.7 pounds per square inch absolute).

V<sub>1</sub>P<sub>1</sub> = V<sub>2</sub>P<sub>2</sub>  
1.0 × 14.7 = V<sub>2</sub> × 19.7  
V<sub>2</sub> = 0.746 ml.

From the divisional volume calibration of the capillary bore the point representing a volume of 0.746 ml. from the stopcock may be accurately picked off on the tube. It is to this point that the mercury will progress under an applied pressure of 5 pounds. Similar calculations are made for 10, 15, or any other desired gage readings.

After the tube is calibrated in gage readings, a scale may be scratched or etched on a sheet of aluminum which can be

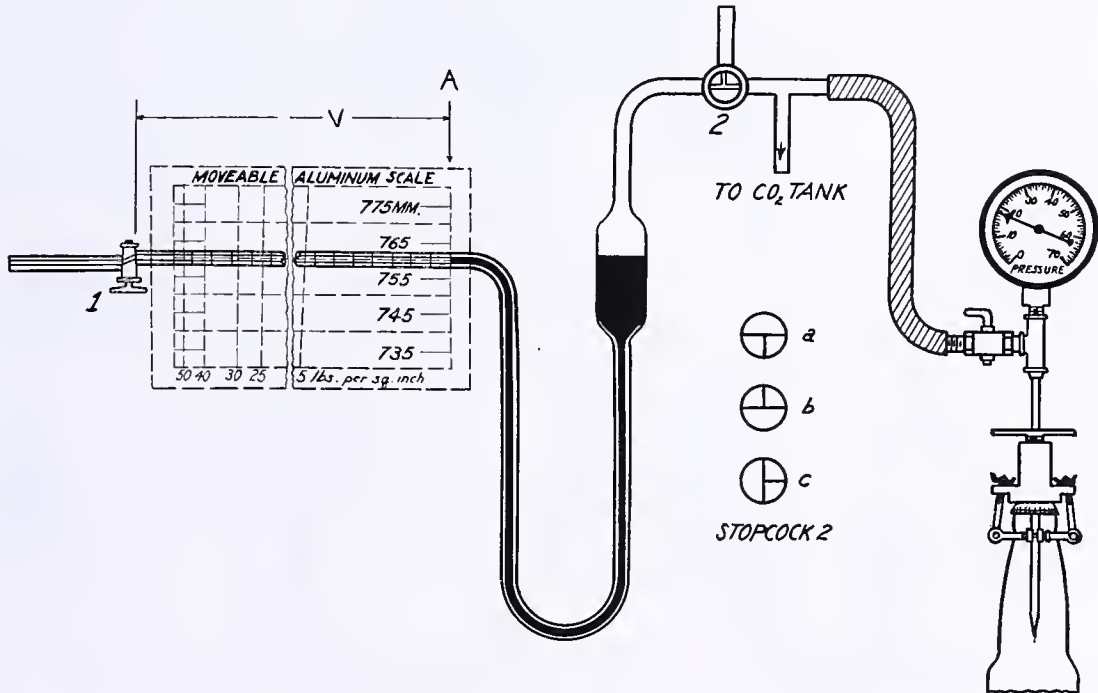


FIGURE 3. MANOMETER FOR CALIBRATING GAGES

<sup>1</sup> Pounds per sq. inch × 0.070307 = kg. per sq. cm.  
<sup>2</sup> For routine work 15 may conveniently be substituted for 14.7.



TABLE II. RECOVERY OF AIR IN AIR DETERMINATION

Expt.	Total Air Ml.	Air Contained in Evolved Gas At 25° C.						Recovery of Air At 25° C.					
		First 100 ml.	100 to 200 ml.	200 to 300 ml.	300 to 400 ml.	400 to 500 ml.	25° to 102° C.	First 100 ml.	To 200 ml.	To 300 ml.	To 400 ml.	To 500 ml.	25° to 102° C.
		Ml.	Ml.	Ml.	Ml.	Ml.	Ml.	%	%	%	%	%	%
1	2.2	1.6	0.1	0.1	0.1	0.1	0.2	73	77	82	86	91	9
2	3.1	2.4	0.2	0.1	0.1	0.1	0.2	77	84	87	90	94	6
3	3.5	2.4	0.2	0.3	0.2	0.1	0.3	69	74	83	89	92	8
4	4.2	3.0	0.3	0.2	0.2	0.1	0.4	72	79	83	88	90	10
5	7.7	5.7	0.3	0.5	0.5	0.2	0.5	74	78	84	91	94	6
6	8.6	6.0	0.6	0.4	0.8	0.4	0.4	70	77	81	91	95	5
7	10.2	7.0	1.0	1.0	0.6	0.2	0.4	69	79	88	94	96	4
8	12.9	10.0	0.7	0.7	0.5	0.4	0.6	78	83	89	92	95	5
9	13.4	12.4	1.0	2.5	0.8	0.6	1.1	67	73	86	91	94	6
10	17.2	13.6	1.1	0.9	0.6	0.4	0.6	79	86	91	94	97	3
11	19.2	15.0	1.4	0.9	1.3	...	0.6	78	86	90	97	97	3
								Av. 73.3	79.5	85.9	91.3	94.2	5.9

conveniently mounted behind the tube. For precise work, several scales may be prepared to cover the range of the varying initial atmospheric pressures as shown in the illustration. For the average gage, however, the multiple scale is not necessary.

The gage is standardized as follows:

Place the apparatus, with the horizontal manometer tube perfectly level, in a position protected from drafts and sudden changes of temperature. Connect the gage to an empty bottle or can, connect also a tank of carbon dioxide equipped with a fine adjustment needle valve as shown in Figure 3. With stopcock 2 in position *a* and stopcock 1 open, apply a slight amount of pressure from the tank to bring the mercury to line *A*. When the mercury reaches this line, close stopcock 1 and release the pressure by bringing stopcock 2 to position *b*. Make a barometric reading of atmospheric pressure and bring the appropriate scale into position behind the tube. Change stopcock 2 to position *a*, and apply pressure from the carbon dioxide tank. When the mercury reaches the 5-pound line make a reading of the gage. Apply more pressure, check the gage against the mercury reading for several pressures, and note any corrections. After the determination is finished, shut off the pressure. Bring stopcock 2 into position *c* to release pressure in the apparatus, and then carefully bring it to position *b* to release pressure slowly in the mercury manometer.

The apparatus is so designed that the correction for varying hydrostatic pressures of mercury is eliminated, which greatly simplifies its use.

Satisfactory results have been obtained in the authors' laboratories over a period of about 3 years, during which time

hundreds of samples of packaged beer have been examined by the above pressure-air method and carefully checking the gages.

### Extent of Air Recovery

Since the influence of air on packaged beer and the importance of its determination have come to be realized, some attempts at distinguishing between "head space," or "free" air, and "dissolved" air have been made from time to time. Actually, of course, this is of only academic interest, since there is a constant absorption of air by the beer from the head space and diffusion into the head space from the beer, depending upon physical conditions. Actual damage to the beer can result only from dissolved oxygen, but the supply of dissolved oxygen is, in turn, replenished from the head space air reservoir of oxygen.

While generally the ideal, in analytical methods, is to accomplish 100 per cent recovery, this is by no means necessary where a constant proportion of the total amount present is always yielded by the procedure. Thus, there would be no point in boiling the beer to recover 100 per cent of air, an inconvenient method, if it could be shown that a fairly constant, large proportion of the total air would always be recovered by shaking at 25° C. As far as its use in correcting the pressure reading for determining carbon dioxide is concerned, complete recovery of the air is not needed, as it is only the head space air that introduces the error, and this is readily

recovered in the first few shake-outs. Even though this question of completeness of recovery of air has no practical significance in the carbon dioxide determination, it is of importance in so far as the question of air control in connection with beer stability is concerned. Therefore, in order to ascertain the extent to which the total air is recovered by the present procedure, the following experiments were carried out:

The apparatus consists of a setup similar to that used for the usual air determination, except that a large gas buret is inserted in the line and the gage is removed, as shown in Figure 4. The use of the gas buret, *C*, permits the removal of measured portions

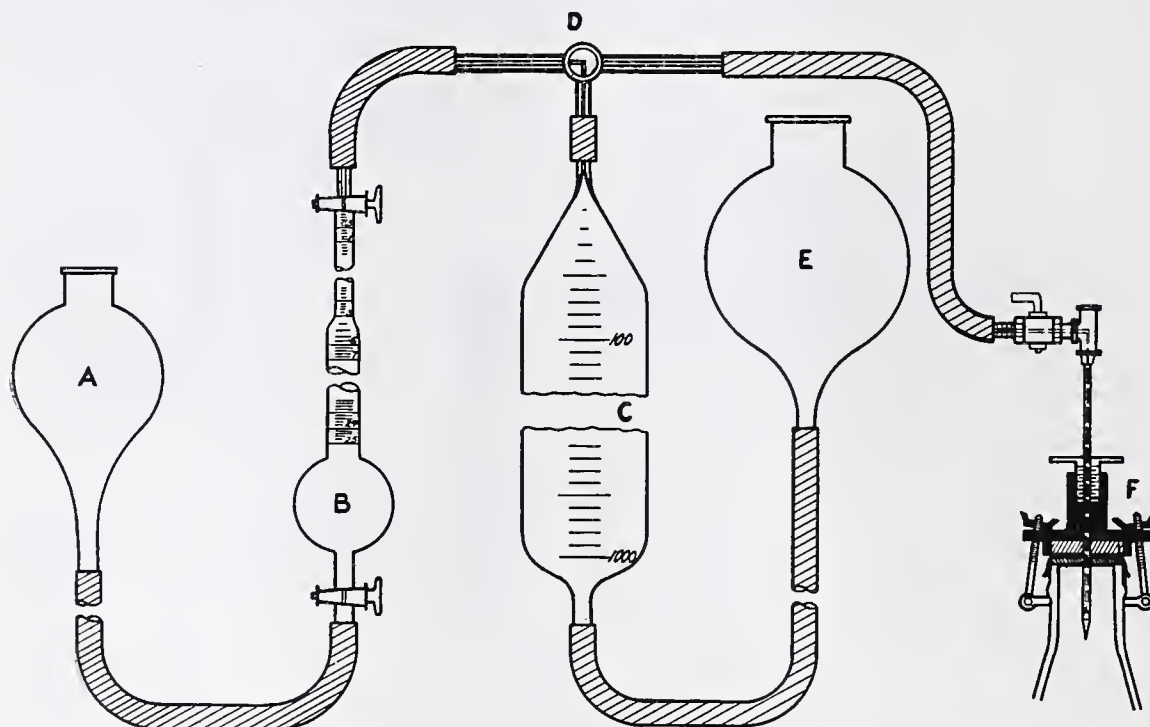


FIGURE 4. DIAGRAM OF APPARATUS



of the air-carbon dioxide mixture from the beer, and these are then analyzed in the alkali buret, *B*.

The absorption buret, *B*, is filled with 15 per cent alkali; gas buret *C* is filled with 20 per cent sodium sulfate solution acidified with sulfuric acid, and contains a few drops of hexyl alcohol. All tubes and connections are rendered air-free by filling with water. The cap is punctured with the spike in the usual manner, and 100 cc. of gas are permitted to flow into buret *C*. Stop-cock *D* is then turned and the 100 cc. of gas are diverted into buret *B*, where the carbon dioxide is absorbed by the alkali and the "air" is measured. Another 100 cc. are permitted to flow into buret *C*, and the process is repeated as long as carbon dioxide is evolved from the beer at 25° C. When all the gas has been evolved at 25° C., the beer bottle is placed in a boiling dilute aqueous-glycerol bath (102° to 103° C.). Leveling bulb *E* is lowered to produce a partial vacuum in *C* and help draw over any gas from the boiling beer. When all the gas has evolved, the gas mixture is moved into *B*, the carbon dioxide is absorbed, and increase in air is noted.

Table II gives the results of these experiments on a number of beers. It will be seen that the bulk of the air (70 to 80 per cent) comes over in the first 100 cc. of the gas evolved from the beer, and that by using ordinary care to evolve as much gas as possible at 25° C., an average recovery of 94 per cent of the total air is possible. It is therefore apparent that this pressure method is not only suitable as an accurate carbon dioxide method, but also gives sufficiently accurate air results for most purposes.

In carrying out the air determination in the usual manner the results may be slightly reduced by reason of the absorption of some of the oxygen in the evolved air by the small amount

of alkaline beer contained in the absorption buret. This error is small and except for the most precise work generally needs no correction.

### Summary

1. A simple, rapid, and precise pressure method for determining carbon dioxide in packaged beer or other carbonated beverages, which corrects for the air error is further described in detail.
2. The method is suitable for the determination of air in packaged beers and carbonated beverages, and is especially valuable for routine control work.
3. The extent of recovery of the air in bottled beers by this method has been determined, and it is shown that an average recovery of 94 per cent may be obtained at 25° C.
4. A simple primary pressure standard for checking the pressure gages is described.
5. An alignment chart for simply calculating the analytical data is presented.

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# Determination of Rotenone in Derris and Cube

## II. Extraction from the Root

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SINCE the publication of the earlier methods for the analytical extraction of rotenone from derris and cube roots using Soxhlet extraction with ether (9) and with carbon tetrachloride (6) as solvents, various other procedures have been proposed. Danckwortt and Budde (4) have used room-temperature extraction with a given weight of chloroform followed by filtration and removal of an aliquot of the filtrate by weight. Cahn and Boam (3) have suggested Soxhlet extraction with trichloroethylene. In a method proposed by Rowaan (10) the sample is extracted at room temperature with successive lots of chloroform. The method of Beach (1) is similar to that of Danckwortt and Budde except that an aliquot of the filtrate is taken by volume. Worsley (12) has used percolation with hot ethyl acetate, and Begtrup (2) proposes percolation with toluene at room temperature. Recently Seaber (11) has presented results by various extraction procedures and has stated Beach's method to be preferable.

The object of the present work was to study some of these methods of extraction and others already in use in the writers' laboratories with a view to deciding on the best procedure to be used in conjunction with the crystallization method already published (7).

### Extraction Methods

It has been known for some time that Soxhlet extraction with carbon tetrachloride for as much as 24 hours does not always completely recover the rotenone. It is also generally

supposed that some of the rotenone may decompose during the long boiling necessary in such an extraction. Accordingly some tests were made of a method partially overcoming this objection in which most of the extract was removed and not subjected to continued boiling. The flask containing the extract was changed after 3 hours and the extraction continued for the usual length of time.

In addition to Soxhlet extraction, four other general methods of extraction were tested:

1. **BOILING-MULTIPLE EXTRACTION METHOD.** The sample was refluxed with the solvent under a condenser on the steam bath for 1 to 2 hours and filtered by suction. The marc was washed on the filter with hot solvent and then refluxed again with fresh solvent, followed again by filtration and washing. This was followed by a third refluxing, filtering, and washing.
2. **BOILING-ALiquOT METHOD.** The sample was treated with a weighed amount of solvent and refluxed under a condenser on the steam bath for 2 to 3 hours. After the solution had cooled to room temperature, solvent was added to replace that lost, until the mixture was brought to its original weight. The extraction mixture was chilled in the refrigerator, filtered through folded filter paper, precautions being taken to prevent loss by evaporation, and an aliquot of the filtrate was taken by volume.
3. **ROOM TEMPERATURE-MULTIPLE EXTRACTION METHOD.** This method was similar to method 1 but was carried out at room temperature.
4. **ROOM TEMPERATURE-ALiquOT METHOD.** This was substantially the method proposed by Beach. The sample was shaken with an accurately measured volume of solvent, the time of shaking ranging from 4 hours to overnight. The remaining procedure was the same as in method 2.



The weight of the sample used in these methods ranged from 10 to 30 grams, depending on the amount of rotenone known to be present. This variation in sample with rotenone content is not necessary but was merely adopted for convenience. The volume of solvent in cubic centimeters used in the aliquot methods was about ten times the weight of the sample in grams. In the multiple-extraction methods this volume of solvent was used for each successive extraction; in the aliquot methods the volume of the aliquot taken was two-thirds that of the original solvent.

In all methods except those using carbon tetrachloride as solvent, after most of the original solvent had been recovered by distillation the extract was evaporated to dryness, taken up in carbon tetrachloride, and again evaporated to dryness. This process was repeated two more times. In the senior author's work the extracts were evaporated to dryness on the

steam bath and then placed under suction momentarily while hot to aid in removal of the solvent. In the junior author's analyses the last 20 to 25 cc. of solvent were evaporated under vacuum.

Occasionally there was extracted by chloroform at room temperature a small amount of material that was insoluble in hot carbon tetrachloride. This occurred more frequently with cube roots than with derris roots. In such cases the carbon tetrachloride solution of the extract was filtered hot and the residue washed thoroughly with hot carbon tetrachloride. Rotenone was then crystallized from the extract in the form of the carbon tetrachloride solvate by the procedure already published (7). As this procedure includes determination of the purity of the solvate by alcohol recovery, the results obtained were for pure rotenone.

The marcs from the multiple extractions were tested for rotenone. They were boiled with acetone for at least one hour and filtered, and the filtrate was evaporated to dryness. This extract was dissolved in an amount of acetone such that 1 cc. was equivalent to 2.5 grams of the original root sample, and portions of this solution were tested by the modified Durham color test (8). Results of the tests were grouped in five grades: 0, negative; 1, faintly positive; 2, medium positive; 3, strongly positive; 4, very strongly positive. It has been the writers' experience that marcs giving tests designated as 1 and 2 do not contain sufficient rotenone to affect the results appreciably. If a test designated as 3 or 4 was obtained, the extraction was not considered satisfactory. The criticism that Cahn and Boam (3) made of the Durham test does not hold here, as in these tests blue-green or green colors, as well as blue, were considered positive. No tests of the marcs from the aliquoting procedures were possible because of the retained mother liquor.

TABLE I. ROTENONE CONTENT OF A SAMPLE OF DERRIS ROOT (No. 3307)

Method	Solvent	Rotenone %	Test of Marc
Soxhlet			
Continuous for 24 hours	Carbon tetrachloride	6.2	3
Flasks changed after 3 hours	Carbon tetrachloride	7.0	3
Boiling-multiple extraction	Benzene	7.1	2
	Carbon tetrachloride	6.4	3
	Chloroform	6.8	1
	Ethylene dichloride	6.9	1
	Trichloroethylene	6.7	2
	Ethyl acetate	6.7	2
	Benzene-alcohol azeotropic mixture	6.9 <sup>a</sup>	0
Boiling-aliquot	Benzene	6.9	..
Room temperature-multiple extraction	Chloroform	7.4	2
Room temperature-aliquot	Chloroform	7.4	..
	Benzene	7.0	..
	Ethyl acetate	7.5	..

<sup>a</sup> Solvate very impure compared with that from other methods.

TABLE II. ROTENONE CONTENT OF POWDERED SAMPLES OF DERRIS AND CUBE

Sample	Chloroform-Room Temperature			Benzene-Boiling			Benzene-Room Temperature-Aliquot	Ethyl Acetate-Room Temperature-Aliquot	Total Benzene Extract	Ratio of Rotenone to Total Extract	Moisture
	Senior author %	Junior author %	Av. %	Analysis %	Test of marc <sup>a</sup>	Analysis %	Test of marc <sup>a</sup>	Aliquot %	%	%	%
Derris											
998	0.5	..	..	..	..	..	..	..	13.4	4	..
999	0.5	..	..	..	..	..	..	..	11.5	4	..
1000	0.6	..	..	..	..	..	..	..	13.0	5	..
2120	8.0	8.0	8.0	8.2	0	7.5	2	..	22.6	35	..
2121	10.0	10.4	10.2	10.3	0	..	..	..	30.4	34	..
2288	0.4	0.4	0.4	..	..	..	..	..	16.2	2	..
2700	4.3	4.6	4.4	..	..	..	..	..	13.6	32	6.7
2701	6.2	..	..	..	..	..	..	..	18.4	34	6.4
2710	3.3	3.2	3.2	..	..	3.2	..	..	15.5	21	5.8
2715	6.0	6.2	6.1	..	..	..	..	..	17.0	36	6.4
2802	2.5	2.7	2.6	..	..	..	..	..	14.0	19	6.7
2803	4.0	3.9	4.0	..	..	..	..	..	13.9	29	6.4
3000	4.3	4.4	4.4	..	..	..	..	..	15.9	28	6.8
3001	5.2	5.5	5.4	5.3	1	5.4	0	5.1	14.8	36	5.7
3002	1.9	2.1	2.0	..	..	2.0	0	..	11.9	17	5.7
3006	3.6	3.6	3.6	..	..	3.7	0	..	15.7	23	6.5
3007	0.5	0.6	0.6	..	..	..	..	..	12.8	5	7.0
3126	5.7	5.9	5.8	5.9	1	5.8	1	5.2	15.7	37	7.2
3307	7.2	7.5	7.4	7.4	2	7.1	2	6.9	19.0	39	5.7
3354	0.7	0.6	0.6	..	..	..	..	..	12.9	5	4.9
3355	3.2	3.6	3.4	..	..	3.4	..	..	10.6	32	7.7
Cube											
2119	5.0	5.1	5.0	..	..	4.7	0	..	19.3	26	..
2664	4.2	4.5	4.4	..	..	..	..	..	13.6	32	7.3
2665	2.4	2.3	2.4	..	..	..	..	..	10.8	22	8.3
2711	1.8	2.0	1.9	..	..	..	..	..	9.4	20	6.7
2714	4.4	4.7	4.6	..	..	..	..	..	13.8	33	7.0
2801	3.6	3.9	3.8	..	..	..	..	..	12.2	31	7.2
3003	2.9	2.8	2.8	..	..	..	..	..	15.9	18	7.4
3004	2.8	3.0	2.9	..	..	2.8	..	..	16.5	18	7.4
3005	5.4	5.7	5.6	5.4	1	5.6	1	4.5	17.6	32	5.6
Timbo											
3230	3.8	4.0	3.9	..	..	3.6	0	..	18.8	21	6.5
3260	4.3	4.4	4.4	..	..	4.6	0	3.2	20.6	21	7.8
Cube											
3449	3.1	3.4	3.2	..	..	..	..	..	7.2	44	8.5
3596	3.7	3.9	3.8	..	..	..	..	..	18.7	20	..
Tephrosia virginiana											
3107	1.3	1.4	1.4	..	..	..	..	..	7.3	19	7.4

<sup>a</sup> 0, negative; 1, faintly positive; 2, medium positive; 3, strongly positive; 4, very strongly positive.



In Table I results are given for a sample of powdered derris root (No. 3307) extracted by these methods with various solvents. As judged by the test on the marcs, the 24-hour Soxhlet extractions with carbon tetrachloride were incomplete. Comparison of the results by the continuous Soxhlet extraction with that in which the flasks were changed indicates that there may have been some decomposition in the continuous extraction. As a further example of the incompleteness of carbon tetrachloride Soxhlet extraction, the marc from one sample of derris root (No. 3095) was found to contain over 1 per cent of rotenone, by subsequent actual extraction and crystallization, after both 24-hour and 48-hour Soxhlet extractions. However, this sample, containing about 8 per cent of rotenone, was the most difficult to extract of all the samples encountered in this work.

In the boiling-multiple extraction method the removal of rotenone as judged by the test on the marc was satisfactorily complete with all solvents tested except carbon tetrachloride. With the benzene-alcohol azeotropic mixture, however, the solvate obtained was of very low purity. The room-temperature extractions with chloroform and ethyl acetate gave results slightly higher than any of the other methods.

At the time this work was begun the boiling-multiple extraction method with benzene was favored. These results indicated, however, that room-temperature extraction might be at least as efficient as the boiling extraction. From the standpoint of ease of handling and avoidance of decomposition the room-temperature extraction undoubtedly was better. Further, the aliquoting procedure seemed convenient and less time-consuming. Accordingly a more detailed study of some of these methods on a large number of samples was undertaken, with particular emphasis on the room temperature-aliquot method using chloroform.

Detailed Examination of Methods

COMPARISON OF ROOM TEMPERATURE-ALIQUOT METHOD WITH OTHER PROCEDURES. Results of analyses made on 35 samples of powdered derris, cube, and Tephrosia roots are given in Table II. That room temperature-chloroform extraction is complete on such samples is shown by the fact that the results agreed with those by the benzene-boiling-multiple extraction method, the marcs from which showed practically complete extraction, and also by the fact that marcs from the chloroform-room temperature-multiple extraction method showed practically complete extraction. That evaporation during filtering and the withdrawal of an aliquot of the filtrate in the chloroform-room temperature-aliquot method

TABLE III. EFFECT OF TIME OF SHAKING UPON THE ROTENONE CONTENT OF A SAMPLE OF DERRIS ROOT (No. 3307)

(Determined by the chloroform-room temperature-aliquot method)

Time of Shaking Hours	Rotenone %
0.25	6.6
0.5	6.6
1	6.8
2	6.9
4	6.8
7	7.0
About 18 (overnight)	7.2

introduce no appreciable errors is shown by the agreement of results with those of the corresponding multiple-extraction method.

TIME OF SHAKING IN THE ROOM TEMPERATURE-ALIQUOT METHOD. Beach's method calls for shaking the mixture of root and solvent for 2 or 3 hours, allowing the mixture to stand overnight, and then shaking for an additional hour. The junior author in most cases adhered to Beach's procedure, using a total of 4 hours' shaking. The senior author, however, used overnight (18 hours) continuous shaking.

To determine the effect of time of shaking on the results, portions of a sample of a powdered derris root (No. 3307) were shaken with solvent for different periods of time, after which each mixture was chilled for 30 minutes and filtered as usual. The results, compared with those for overnight shaking, are shown in Table III. It might appear that in general more rotenone was extracted during the longer periods of shaking, but the differences are so small that for practical purposes equilibrium might be considered to have been reached in about 2 hours. For convenience, however, and to ensure complete extraction, the overnight shaking seems preferable.

EFFECT OF FINENESS OF THE SAMPLE. The chloroform-room temperature-aliquot procedure has been shown to be satisfactory for powdered samples. The manufacturers who supplied these samples claim to be grinding so that about 90 per cent will pass a 200-mesh sieve. At any rate, these samples were sufficiently fine so that 100 per cent passed a 60-mesh sieve. When, however, this method, with overnight shaking, was applied to certain more coarsely ground samples, the results were disappointing.

Table IV shows the results for such samples, together with the fineness in terms of the percentage passing a 60-mesh sieve.

In a number of these samples results by the chloroform-room temperature-aliquot method were markedly lower than those by the chloroform-room temperature and benzene-

TABLE IV. ROTENONE CONTENT OF COARSELY GROUND SAMPLES OF DERRIS AND CUBE

Sample	Passed 60-Mesh %	Before Regrinding— Rotenone Content								After Regrinding— Rotenone Content				Total Benzene Extract %	Ratio of Rotenone to Total Extract %		
		Chloroform— Room Temperature— Multiple Extraction			Benzene-Boiling Multiple Extraction			Chloroform-boiling- aliquot %	Ace- tone- room tem- pera- ture- aliquot %	Ethyl acetate- room tem- pera- ture- aliquot %	Chloroform—Room Temperature Multiple Extraction						
		Aliquot %	Analysis %	Test of marc <sup>a</sup>	Analysis %	Test of marc <sup>a</sup>	Aliquot %				Test of marc <sup>a</sup>	Passed 60-mesh %	Aliquot %			Analysis %	Test of marc <sup>a</sup>
Derris																	
3095	98	5.2	8.2	0	7.7	0	6.9	..	..	..	..	..	..	17.1	48		
3493	85	4.4	5.9	0	5.2	3	4.5	..	..	..	93	5.2	..	14.0	42		
3494	87	6.6	7.0	0	6.4	1	6.0	..	..	..	98	6.2	..	16.3	43		
3495	90	6.4	10.2	1	9.2	4	8.0	8.6	7.6	..	98	9.1	..	21.7	47		
3496	83	8.9	9.9	3	9.7	3	8.6	..	..	..	97	9.4	9.8	24.3	41		
3584	95	4.0	..	..	4.0	0	..	..	..	..	..	..	..	13.2	30		
3594	57	5.8	5.9	1	5.5	2	..	..	..	5.5	..	..	..	15.8	37		
Cube																	
686-A	90	10.9	10.9	1	10.7	1	.	..	..	..	..	..	..	24.7	44		
Timbo																	
2504	40	8.8	11.0	4	9.8	4	9.6	9.0	9.2	..	90	9.6	11.6	28.3	39		
2505	46	3.6	5.3	3	4.4	3	4.7	..	..	..	97	4.5	..	16.3	32		
Cube																	
3595	71	1.5	..	..	1.1	1	..	..	..	1.5	..	..	..	9.8	11		

<sup>a</sup> 0, negative; 1, faintly positive; 2, medium positive; 3, strongly positive; 4, very strongly positive.



boiling-multiple extraction methods, even where extraction by the last two methods was unsatisfactory. Some of the samples showing this incomplete extraction were reground in a Wiley laboratory mill and again analyzed, with the results also shown in Table IV. Results by the chloroform-aliquot method were in general higher than before regrinding but were still lower than those by the chloroform-multiple extraction method before regrinding. Two of the samples which were among the most difficult to extract were analyzed by the chloroform-multiple extraction method after being reground and extraction was found to be slightly more complete than before regrinding, as judged by the tests on the marc. These results definitely demonstrate that on coarse samples such as these more complete extraction is obtained by the chloroform-multiple extraction method than by the aliquot procedure.

That coarseness of the sample alone does not necessarily lead to incomplete extraction is shown by some of the results in Table IV. Thus, sample 3594, which was very coarse, gave satisfactory results by the chloroform-room temperature-aliquot method as judged by comparison with results by the benzene-boiling-multiple extraction method and the chloroform-room temperature-multiple extraction method. On the other hand, sample 3095, which was considerably finer, gave markedly low results by the first method.

It is evident from the results in Table IV that, regardless of the method used, samples must be finely ground to give complete extraction. Probably a sample should be ground so that at least 95 per cent of it passes a 60-mesh sieve. Grinding to this fineness may be accomplished in the Wiley laboratory mill. When the usual run of samples is ground to this fineness, it may be expected that satisfactory extraction will be obtained by the chloroform-aliquot procedure. If, however, the rotenone content is unusually high, as discussed in the next section, or for any other reason there is doubt as to the completeness of extraction, the analysis should be made or checked by the chloroform-multiple extraction method. The results obtained here indicate that this method, although less convenient and more time-consuming than the aliquot procedure, can be relied upon to give complete extraction if the sample is ground to the fineness specified.

**EFFECT OF RATIO OF ROTENONE TO TOTAL EXTRACT ON COMPLETENESS OF EXTRACTION.** Sample 3095, which although finer than some of the other samples did not give complete extraction by the chloroform-room temperature-aliquot method, had the highest ratio of rotenone to total extract of any of the samples studied.

Likewise sample 3495, in which the ratio of rotenone to total extract was also high, gave unsatisfactory results by the same method, even after regrinding to the fineness of sample 3095. In calculating this ratio the value for rotenone by the chloroform-room temperature-aliquot method was used for the powdered samples, and that by the chloroform-room temperature-multiple extraction or the benzene-boiling-multiple extraction method for the coarsely ground samples. Benzene extractives were determined by Soxhlet extraction of 5-gram samples. In general, the amount of total benzene extractives appears to be about the same as that of the total ether and total chloroform extractives. Some evidence has already been obtained, in making Soxhlet extractions of small samples for total extractives, that, even among the powdered samples, those containing the higher percentages of rotenone were more difficult to extract. This may explain the unsatisfactory results on the two samples mentioned. It is possible that, if these samples could have been ground to the degree of fineness of the finely powdered samples in Table II, complete extraction by the aliquot procedure might have been obtained. Equipment for accomplishing this with small samples is not readily available, and in lieu of this it seems that samples should be checked by the chloroform-room

temperature-multiple extraction method when the ratio of rotenone in the total extract is about 40 per cent or over. Such samples are unusual, however. In a recent article reporting the analysis of 190 samples of derris root, Georgi (5) found the maximum ratio of rotenone to total extract (ether) to be 39 per cent.

**RELATIVE EASE OF EXTRACTION OF DERRIS AND CUBE.** In general cube and timbo roots are much more readily extracted of their rotenone content than is derris root. Thus, in Soxhlet extractions of small samples most solvents completely extract the rotenone from cube and timbo whereas many of these solvents do not give complete extraction of derris roots, as indicated by color tests of the marcs. The results in Table IV for cube root 686-A, a sample of only medium fineness in which the ratio of rotenone to total extract was very high, indicate that these factors are not so serious in causing incomplete extraction as in the case of derris roots.

It was observed that at 0° C. the solvate crystallized more slowly from cube extracts than from derris extracts of comparable rotenone content.

### Accuracy and Precision of Methods

No attempt was made to study the accuracy of the extraction procedures. Because of the practical impossibility of determining the exact amount of rotenone in a given root by any method now available, such a study would be difficult and unsatisfactory. It can only be stated that on the powdered samples studied the chloroform-room temperature and the benzene-boiling-multiple extraction methods seem to give satisfactorily complete extraction and that, since results by the chloroform-room temperature-aliquot method agree with these, it may also be presumed to give satisfactory extraction.

Only the chloroform-room temperature-aliquot method was studied extensively enough to permit a definite conclusion as to precision. Replicate results on a sample by a single investigator in general agreed within about 5 per cent. Results by the junior author were in general slightly higher than those obtained by the senior author (Table II).

At various points in both the extraction and the crystallization the procedures used by the two authors were slightly different. Thus in the extraction the senior author used overnight shaking, while the junior author used a total of 4 hours' shaking interrupted in most cases by overnight standing. In a few determinations the junior author did not chill the extracts before filtering. The chilling of the original mixture before filtration seems advisable from another standpoint than merely to prevent loss by evaporation. It was found that in some cases in which this preliminary chilling was not made the filtration of the solvate at 0° C. was slow and difficult, whereas the solvate from the same sample filtered readily when the chilling was employed. Evidently the preliminary chilling separates waxes or resins from some samples that would otherwise separate during the crystallization at 0° C. and interfere with the filtration of the solvate. The senior author used the vacuum after each evaporation of the extract in the earlier analyses, whereas the junior author made the entire evaporation under vacuum in all cases. For the crystallization the senior author added a volume of carbon tetrachloride numerically equal in cubic centimeters to the weight of the sample in grams, while the junior author made the extract to this total volume by the addition of carbon tetrachloride.

The average difference between the results by the two authors was only about 3.5 per cent. In view of the many slight differences in procedure, the two sets of results may be considered to be in good agreement. In general it would seem that results by two investigators should agree within about 5 per cent.



### Moisture Content of Powdered Derris and Cube Roots

In Table II are given the values for moisture content of the powdered derris and cube roots determined by drying 2-gram samples at 106° C. for 2 hours. Two days' additional drying of some of the samples caused no significant additional loss in weight. It will be noted that the values range only from 4.9 to 8.5 per cent. In view of this small variation the rotenone values have not been corrected for moisture content of the sample.

Work done in the writers' laboratories indicates that it is preferable not to dry the sample before extraction. In cases in which a preliminary drying has been made the results for rotenone and the purity of the separated solvate have usually been slightly lower than on the undried root. There are indications also that drying renders extraction more difficult. Some samples were dried at 100° C., and others at 50° C. under vacuum. It is possible that drying at room temperature, such as in a vacuum desiccator, would not interfere with the rotenone determination. Such drying, however, seems unnecessary for the analysis of the usual samples received in this country.

### Summary and Conclusions

In the analysis of finely powdered samples of derris and cube roots a method involving treatment with chloroform at room temperature followed by removal of an aliquot of the filtered extract gives satisfactorily complete extraction of the rotenone.

Fineness of the sample is an exceedingly important factor in obtaining complete extraction by any method. If coarse samples are ground so that at least 95 per cent passes a 60-

mesh sieve, they will usually give satisfactory extraction by the aliquoting procedure.

Samples containing a high ratio of rotenone to total extractives were found to be more difficult to extract than those with lower percentages of rotenone. When the ratio of rotenone to total extract was about 40 per cent or over, particularly in the case of derris roots, it was necessary to employ extraction at room temperature with successive lots of chloroform in order to obtain satisfactory extraction of the rotenone. This method should also be employed as a check whenever there is doubt as to the completeness of extraction by the aliquoting procedure.

Cube roots in general are more readily extracted of their rotenone content than are derris roots.

The moisture content of derris and cube roots as received in this country has not been found to be sufficiently great to interfere with their analysis, and hence preliminary drying of samples seems unnecessary.

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## Standardizing Silver Nitrate Volumetric Solution

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THE author has used to good advantage the following short method for the standardization of volumetric silver nitrate.

A volumetric hydrochloric acid solution is exactly neutralized, using a standard alkali solution. The chloride salt formed is then determined by titrating with a volumetric, silver nitrate solution, using potassium chromate as indicator. The number of cubic centimeters of hydrochloric acid is exactly equivalent to the number of cubic centimeters of standard alkali, which, in turn, is exactly equivalent to the number of cubic centimeters of silver nitrate. Thus, if any one of the above is known, the other two can be determined.

The author used this method to standardize silver nitrate against sodium hydroxide standard volumetric solution, for chloride determinations. Sodium hydroxide was used as the standard in preference to hydrochloric acid, since in this particular laboratory standard hydrochloric acid was not available as a stock reagent.

Place 25 cc. of 0.1 N hydrochloric acid, accurately measured from a buret, and about 25 cc. of distilled water in an Erlenmeyer flask of about 200- to 300-cc. capacity. Using phenol-

phthalein test solution as indicator, titrate to a faint pink with the standard 0.1 N sodium hydroxide volumetric solution. Add 2 cc. of a 5 per cent potassium chromate test solution and titrate with the silver nitrate solution, to the first red tinge. The cubic centimeters of silver nitrate, consumed in the titration, are exactly equivalent to the cubic centimeters of the standard sodium hydroxide.

When checked against the thiocyanate volumetric method and the silver chloride gravimetric method, good results were obtained and the time required was only a few minutes as against hours in these two other methods.

This principle can also be applied to the standardizations of potassium permanganate and oxalic acid volumetric solutions, by neutralizing the volumetric oxalic acid with the standard alkali, and determining the oxalate salt formed by titration with the potassium permanganate solution. The only precaution here is to use a nonreducing indicator in the oxalic acid-alkali titration, so that it will have no effect on the subsequent permanganate titration. It follows that the cubic centimeters of oxalic acid are exactly equivalent to the cubic centimeters of standard alkali and of permanganate.

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# Determination of Magnetic Iron Oxide

## As a Measure of Corrosion of Boiler Superheater Elements

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SINCE the advent of the use of high pressures and temperatures in steam boilers and superheaters, much work has been done on methods for determining the rate of corrosion of steel by steam at elevated temperatures (3, 6). Most of these methods involve a determination of the amount of magnetic iron oxide which forms on parts of the equipment during operation. Unfortunately, however, a rapid, accurate method has not been available for such determinations.

Methods dependent on the reduction of magnetic iron oxide to metallic iron by carbon (2), hydrogen (5), or carbon monoxide (7) require complicated apparatus and are time-consuming, and often the reduction is incomplete. The same is true of methods employing electrolytic reduction (4) and of those involving the weighing of the water formed on reduction of the oxide.

The present work was undertaken with a view to developing a simple, rapid, and accurate method for the determination of magnetic iron oxide on superheater tube specimens.

For some time concentrated hydrochloric acid containing antimony and stannous chloride has been used for removing rust ( $\text{Fe}_2\text{O}_3$ ) from ferrous specimens (1). The rust dissolves rapidly, leaving clean specimens which may be inspected or weighed. No data were available, however, on the use of this solution for the removal of magnetic iron oxide ( $\text{Fe}_3\text{O}_4$ ) from ferrous specimens.

In the method described, the magnetic iron oxide on specimens of superheater tubes is determined by finding their loss in weight when immersed in an inhibited acid solution having the same composition as that commonly used for rust removal (1):

	Parts by Weight
Concentrated hydrochloric acid	100
Antimony oxide	2
Stannous chloride	5

### Experimental

The length of time required to remove the magnetic iron oxide completely from the inner surface of pieces of superheater tubes was first determined. The specimens were thoroughly cleaned on the outside by grinding and were then washed with benzene. After drying and weighing, they were suspended in the inhibited acid solution described above. The solution, which was at room temperature and contained in glass beakers, was vigorously stirred during the immersion period. The specimens were removed at 5-minute intervals, washed with distilled water, and brushed with a fine bristle brush, after which they were again washed with distilled water and finally dried and weighed (Table I).

TABLE I. LOSS IN WEIGHT OF A TYPICAL OXIDE-COVERED SUPERHEATER TUBE SPECIMEN (S. A. E. 6120 STEEL)

Time Min.	Weight of Specimen Grams	Cumulative Loss in Weight Gram
0	57.4084	
5	57.2281	0.1803
10	57.0803	0.3281
15	57.0025	0.4059
20	56.9941	0.4143
25	56.9913	0.4171
30	56.9904	0.4180
35	56.9900	0.4184

Next the loss in weight of oxide-free specimens, due to reaction of the steel with the solution, was determined. The magnetic iron oxide and scale were removed from the outer and inner surfaces of superheater tube specimens by grinding, after which they were given the same treatment as the specimens covered with oxide. Typical results of such tests for two different steels are given in Table II.

Finally, the amount of magnetic iron oxide was determined on specimens obtained from different sections of superheater tubes.

TABLE II. LOSS IN WEIGHT OF OXIDE-FREE SUPERHEATER TUBE SPECIMENS

Time Min.	Total Loss in Weight	
	S. A. E. 6120 Cr-V steel G./sq. dm.	A. S. T. M. Spec. 83 low-C steel G./sq. dm.
0		
5	0.00327	0.00415
10	0.00429	0.00488
15	0.00503	0.00527
20	0.00547	0.00567
25	0.00591	0.00572
30	0.00649	0.00586

These specimens, after having been cleaned and weighed, were immersed in the solution for 30 minutes, after which they were cleaned and weighed as described above. The total loss in weight was corrected for the solvent action of the solution on the exposed unoxidized steel according to the results given in Table II. The net loss in weight for each of these specimens is given in Table III.

TABLE III. MAGNETIC IRON OXIDE PRESENT ON SUPERHEATER TUBE SPECIMENS

Type of Metal	Magnetic Iron Oxide Present G./sq. dm.
6120 Cr-V steel	1.709
A. S. T. M. Spec. 83 low-C steel	1.369
6120 Cr-V steel	1.171
6120 Cr-V steel	2.242

The results in Table I show that the loss of weight became practically constant in 30 minutes, indicating that the magnetic iron oxide was completely removed from the superheater tube specimens. The slight loss in weight after this time was due to a reaction of the solution with the oxide-free specimens. As shown in Table II, the total loss in weight of the oxide-free specimens of the two steels tested was very small for the 30-minute immersion period, and the portion lost after 15 minutes was negligible. In most cases, any correction for the solvent effect of the solution on the oxide-free steel may be disregarded but, if such a correction is necessary, the values given in Table II may be used. The results given in Table II show that there was very little difference in the total loss in weight of the oxide-free specimens of the two types of steels tested, indicating that the method may be applicable to more than one type of low alloy steel.

The results given in Table III are believed to be very accurate because, in all cases, the magnetic iron oxide was rapidly and completely removed from the specimen, and the loss in weight of the specimen due to reaction of the steel with the solution amounted in most cases to only about 0.3 per cent of the total loss in weight. Moreover, this loss of weight, and hence the correction, was constant.

The hydrochloric acid-antimony oxide-stannous chloride solution may be used repeatedly, but should be discarded when it becomes yellow.

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# Standardization of 2,6-Dichlorophenolindophenol

## An Improved Method

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SEVERAL methods have appeared in the literature for the standardization of 2,6-dichlorophenolindophenol solution as used in the chemical method for the determination of ascorbic acid. Basically these methods all require the standardization of lemon juice or a solution of ascorbic acid against a standard iodine solution, followed by the standardization of the dye against either the lemon juice or the ascorbic acid solution.

There are several objections to the use of such a method. Among these are the instability of the iodine solution, the necessity of preparing fresh lemon juice or fresh ascorbic acid solution every day, the problem of interfering substances when lemon juice is used, and the difficulty at times encountered in obtaining a satisfactory end point.

The method presented here is designed to minimize these disadvantages.

For the purpose of this study, dye solutions were prepared as follows:

The desired quantity of dye (35 to 70 mg. per 100 ml. of solution) is placed in a small beaker and successive portions of hot water are added. After each addition of water the solution is decanted through a filter into a volumetric flask, and when all the dye has been dissolved the filter is washed with small portions of hot water until the washings are colorless or nearly so. After cooling to room temperature, the solution is made up to volume.

Fifteen milliliters of the dye solution are pipetted into a 50-ml. Erlenmeyer flask, 0.5 to 1.0 gram of potassium iodide and 0.5 to 1.0 ml. of dilute sulfuric acid (1 to 4) are added, and, after shaking to facilitate the oxidation of the potassium iodide, the liberated iodine is titrated with 0.01 *N* sodium thiosulfate using the usual starch indicator.

It has been established that 1 ml. of 0.01 *N* iodine solution is equivalent to 0.88 mg. of ascorbic acid; consequently, 1 ml. of 0.01 *N* sodium thiosulfate solution should also be equivalent to 0.88 mg. of ascorbic acid. This has been found to be the case.

### Editor's Note

An unusual coincidence has arisen with respect to the work of Menaker and Guerrant and of Buck and Ritchie on the standardization of 2,6-dichlorophenolindophenol, which is here recorded.

The paper by Menaker and Guerrant was received in the office of INDUSTRIAL AND ENGINEERING CHEMISTRY on September 6, 1937. On September 15 we received a paper by Buck and Ritchie, which had been presented at the Rochester Meeting of the AMERICAN CHEMICAL SOCIETY and an abstract of which had been sent to the secretary of the Division of Biological Chemistry on July 17, 1937, and had been included in the planographed abstracts of the meeting which were given premeeting publicity on August 23.

Priority for the published disclosure must be given to Buck and Ritchie in so far as the abstract, printed here, gives the information. We are printing the paper of Menaker and Guerrant in full, however, inasmuch as it was received first in this office and before actual presentation of the other paper at Rochester.

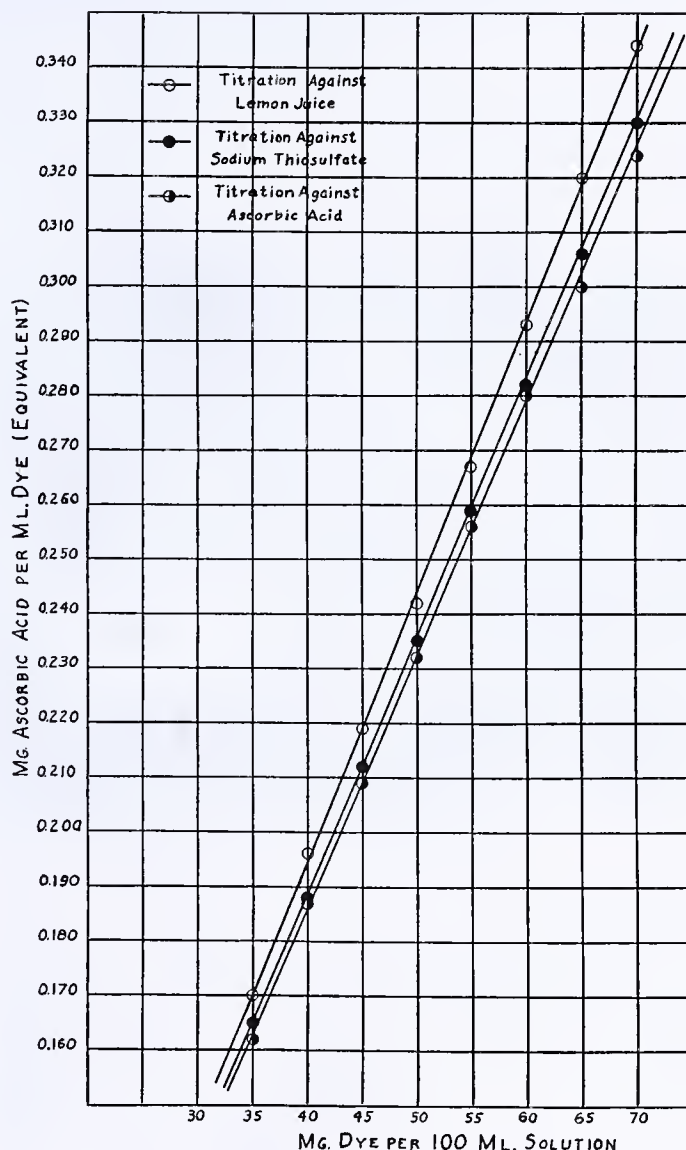


FIGURE 1

Figure 1 represents the data obtained by titrating different concentrations of the dye solution against lemon juice, ascorbic acid, and sodium thiosulfate.

### Discussion

The curve obtained for the titrations against sodium thiosulfate is comparable with that in which ascorbic acid was used, but is somewhat lower than that obtained with lemon juice. This leads to the conclusion that lemon juice contains small amounts of substances other than ascorbic acid which are oxidized by iodine but not by the dye.

The following equations were obtained by application of the method of least squares to determine the best straight line for each series of points:

$$\begin{aligned}\text{For titration against lemon juice,} \\ y &= 0.004964x - 0.005 \\ \text{For titration against ascorbic acid,} \\ y &= 0.004610x + 0.002 \\ \text{For titration against sodium thiosulfate,} \\ y &= 0.004711x\end{aligned}$$



It is interesting to note that the  $y$  intercept of the curve representing titrations against sodium thiosulfate is zero.

The chief advantages of the proposed method are: The sodium thiosulfate solution remains stable after it has once reached equilibrium; the end point of the titration is sharp as contrasted to the blue-to-pink-to-colorless end-point change

observed in the previous methods; and since standard sodium thiosulfate solution is normally required as a check on the standard iodine solution used in either of the other methods, the need for one of the usual standard solutions (the iodine solution) has been eliminated.

RECEIVED September 6, 1937.

## A New Method for the Standardization of the Dye Used for the Determination of Cevitamic Acid (Vitamin C)

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THE new method which is presented is based on the fact that the dye, 2,6-dichlorophenolindophenol, will quantitatively oxidize iodide to iodine. The iodine liberated can then be determined by titration with standard sodium thiosulfate. This method is not only simpler in procedure than other methods, but also gives more accurate results. The results agree very closely with those obtained when pure cevitic acid is used as the standard.

ABSTRACT of paper presented before the Division of Biological Chemistry at the 94th Meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937. Copy of abstract received by A. C. S. News Service July 30, 1937.

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## Photographing Line Tests in Vitamin D Assays

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THE photographing of experimental results is by no means unusual in the field of vitamin D assays or in other lines of work. Stevens and Nelson (3) and Bacharach, Allchorne, Hazley, and Stevenson (1) have reported the methods used in their laboratories for this purpose. The methods of these two groups of workers are fundamentally the same in that individual rat bones are photographed under a microscope with lens equipment which gives approximately  $5 \times$  magnification. The method described in this paper permits the photographing of as many as 80 single radii on one  $12.5 \times 17.5$  cm. ( $5 \times 7$  inch) film or plate at a  $2 \times$  magnification and is believed to be much more economical than those previously described, both in materials and in the time required for the photographic processes. The results which may be obtained with this method are shown in Figure 1, which is a portion of a typical photograph of the actual size used—that is,  $2 \times$  magnification.

### Fixing and Staining Bones

Although this paper is primarily concerned with the photographic technic, brief mention will be made of the prior treatment of the bones, since this treatment may influence slightly the final results. The method is, in general, very flexible and many modifications are possible.

At the end of the assay period, the animal is killed and the desired portions of the bones to be examined are removed and fixed in 95 per cent ethyl alcohol. It is preferable to allow the bones to remain in the alcohol for at least 24 hours for complete

clearing, although this process may be hastened somewhat by splitting the bones before immersion in the alcohol. If an assay is not brought to completion in one day or if, for any other reason, it is not convenient to make the photographs at the time of killing, the bones may be left in alcohol for an extended period of time. It was found, for example, that the photograph of a group of left radii, made after the bones had been stored for one year in 95 per cent alcohol, showed calcification practically identical with that shown by the picture of the corresponding right radii, made immediately after fixation. The use of lower concentrations of alcohol is not advised, since it was found impossible to obtain satisfactory staining in the case of a few bones which had been stored in 70 per cent alcohol for less than 2 months. Ten per cent formalin is used by some workers as a fixative, but alcohol is preferred in this laboratory because it is not as unpleasant to handle, it yields a bone which is somewhat better for photographing, contrary to the observations of Bacharach et al., and the possibility of the leaching out of calcium salts by the more aqueous medium is avoided. Although no data have been obtained, the leaching effect might become noticeable if sufficient acidity developed from the formalin.

It has been the practice in this laboratory to use only the distal end of the radius in making the line-test readings. However, since the radius and ulna are connected, the distal ends of the two bones are allowed to remain attached during the alcohol fixation. The most convenient procedure is to remove the distal ends of both sets of radii and ulnae, free the bones from the greater portion of adhering tissue, and tie both sets to a small paper tag bearing the rat number. The tying is done in such a way that one set of bones may very readily be removed, leaving the other set still labeled. This second set may be preserved for at least a year for possible future work.

The bones are split and stained according to the regular procedure, except that care is taken to avoid overstaining. Usually from 50 to 80 bones are treated at one time. As each bone is split, it is immersed in water to remove most of the alcohol. As soon as all the bones are split, the water is replaced by 1.5 per cent silver nitrate and the bones are stained by exposure to the

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ordinary diffused light of the laboratory. This lighting is recommended, since it gives a slow rate of staining and permits closer control of the depth of staining. Under the usual lighting conditions the bones darken sufficiently in 5 to 10 minutes. If the action is not rapid enough it may be hastened by means of artificial light. Actinic light, such as direct sunlight, a carbon arc, or one of the so-called sun lamps, will give very rapid staining, but has no particular advantage otherwise.

As soon as the bones have stained so that a distinct, light-brown image of the calcified areas can be seen, the silver nitrate is poured off and the bones are washed with three changes of distilled water. When treated in this manner the bones will darken only slowly on further exposure to light and, if protected from light by a layer of heavy paper, may be kept for 2 to 3 days prior to reading or photographing. If, however, the photographing is to be done immediately, it may be advisable to leave the bones in the silver nitrate until the staining becomes heavier. In some laboratories it is the practice to treat the stained bones with ordinary photographic hypo (sodium thiosulfate) in order to prevent further darkening, especially in the noncalcified areas, but in this laboratory the process has proved to be somewhat erratic. Since excellent results may be obtained without this step, its use is not recommended.

Photographic Equipment

For photographing, the authors use a Bausch & Lomb type H vertical photomicrographic camera equipped with a Bausch & Lomb f 1:4.5 Microtessar lens of 48-mm. equivalent focus and a compound shutter. This equipment gives a minimum of two and a maximum of ten diameters enlargement. Most of the work in this laboratory is done at the smallest degree of enlargement, since this allows a large number of bones to be photographed on one negative and at the same time yields a picture of the individual bones which shows adequate detail for the line-test readings. If larger pictures are desired it is comparatively easy to make photographic enlargements from the original negative.



FIGURE 1. ACTUAL SIZE OF LINE-TEST PHOTOGRAPHS

Both Stevens and Nelson (3) and Bacharach and co-workers (1) use an optical system which yields a 5 × magnification. It is stated by Stevens and Nelson that this permits sufficient enlargement for precise interpretation. However, it would seem that such precision is not significant when dealing with a single rat bone. This is particularly true when the line of calcification is only partially formed, as then the calcification often occurs in irregular clumps. If such a bone is split near

the edge of one of these clumps, the clump often remains intact, all of it appearing on one side and none on the other side of the bone. This may result in markedly different readings on the two sides of the same bone. Furthermore, it is apparent that, for the same reason, several sections through different parts of a single bone may give quite different pictures. Added to this fact, one has what may be called the normal variations of experimental animals. Hence, it would seem impossible to draw precise interpretations on the basis of a single line-test reading, and, although the use of such precision would not cause any additional error, it would not introduce further accuracy.

It is much more important that the treatment of the bones be as consistent as possible so that, if errors are present in the line readings of one group, the same errors in the same direction will be present in the readings of all the other groups.



FIGURE 2. APPARATUS FOR HOLDING SPLIT AND STAINED BONES FOR PHOTOGRAPHING

For example, it is the practice in this laboratory, when the two sides of a bone show different amounts of calcium, always to photograph and read that half of the bone which gives the higher reading. Similarly, all the bones should be stained as equally as is possible and all bones should be photographed at the same degree of enlargement.

Arranging Bones for Photographing

When the bones have become properly stained, the line tests may be read directly or the bones may be photographed and the readings made from the print. It is advisable to take at least one set of readings on the bones to guard against the possibility of the disarrangement of their order.

For photographing, the bone sections are arranged in rows on a piece of blotting paper, backed by a glass plate, and are covered with another piece of glass, as shown partially in Figure 2. If large bones, such as the tibia, are to be photographed, additional layers of blotting paper may be advisable as a cushion to compensate for uneven thicknesses of the bones. The sandwich thus formed is held together by rubber bands wound around each end. Unless there are marked differences in the thicknesses of the bones, no difficulty should be experienced in keeping all the bones in place. Using 2 × magnification on a 12.5 × 17.5 cm. (5 × 7 inch) film one may photograph an area of 6.25 × 8.75 cm. (2.5 × 3.5 inches). However, in order to provide a slight margin of safety so that all the bones will appear on the film, it is better to have the glass plate slightly smaller than the latter area. Lantern slide cover glasses cut in half to furnish an area 5 × 8.125 cm. (2 × 3.25 inches) are excellent for this purpose. It is possible to arrange 8 rows of 10 radii each on this size of plate, and also to have space for writing the legends.





FIGURE 3. APPARATUS FOR PHOTOGRAPHING LINE TESTS

The color of blotting paper used as a backing for the bones is a matter of individual choice. In this laboratory white is used; other workers prefer black. Possibly gray would be better than either, since it would contrast with both the white of the noncalcified area and the black of the calcified portion of the bones. No attempt is made to incorporate any legend with the actual bones. However, as shown in Figure 2, strips of black paper, 2 to 4 mm. wide, are placed on the blotting paper so that a strip occurs between each row of bones. The black strips appear as clear strips on the negative and furnish an ideal place for writing the rat number, line-test reading, and any other necessary information. This material is written on the reverse or shiny side of the film with India ink, using a fairly fine pen point, and appears as white letters on a black background in the final picture. In addition, a portion of a thin metric ruler is placed under the cover glass at one end of the assembly so that the degree of enlargement may always be verified. All the bones of a single test are arranged on one line, so that it is very easy to cut the print into strips.

After the bones have been arranged and the cover glass has been fastened in place, the whole assembly is slowly immersed edgewise in a Petri dish of distilled water, care being taken that no air bubbles are trapped between the glass plates. Sufficient water is then added to cover the upper glass surface completely, in order to eliminate the glass-air surfaces which might cause undesirable reflections. The use of a polarizing screen (sold under the trade name Pola Screen) to lessen reflections in large areas or from tiny spots has been recommended (2). However, little difficulty should be experienced, if the direct rays from the lights strike at an angle which does not reflect into the lens. The screen might prove to be of value if extremely fine detail were desired in the picture.

### Lighting

The light source should be fairly brilliant for ease in focusing and well diffused, since the black and white of the bone surface is the only thing of interest. The practice in this laboratory is to use two 60-watt bulbs in small reflectors, which are supported by a ring stand and clamps so that a light is on opposite sides of, and at the same height as, the camera lens. This arrangement gives some shadows, especially between the bones, but they are not confusing. The complete equipment, including the lights, is shown in Figure 3. Additional lights might be used to form a complete ring which would yield a stronger light with less shadow effect, but the advantages do not seem commensurate with the work required.

### Photographic Technic

With the bones in place and the lights adjusted, the image is focused on the ground glass with the lens diaphragm wide open.

The usual method of focusing is by means of a focusing mount which carries the lens, but in most of the work in this laboratory it has been considered desirable to make all the photographs at a fixed degree of enlargement. Hence, the position of the camera and lens is kept exactly the same and focusing is accomplished by moving the object to be photographed. For this purpose a table, adjustable in height, made by fastening a light board to one of the cup holders of a discarded colorimeter, has been found convenient. It is, of course, important that the improvised support be perpendicular to the axis of the camera and lens in order to avoid distortion of the image.

After focusing, the lens diaphragm is shut down to  $f_{11}$ , the film holder inserted, and the picture is taken. With most lenses there is no point to stopping down the lens further, since the resolving power of lenses tends to decrease with small diaphragm openings. The correct exposure is important, but since it will vary with the type of film, the intensity of the light source including the general illumination of the room, the degree of enlargement, and the object being photographed, no definite time can be given. However, as a guide, with two 60-watt lights in small reflectors about 15 cm. (6 inches) from the object, using commercial panchromatic cut film, and enlarging  $2\times$ , an exposure of 10 seconds at stop  $f_{11}$  has been found adequate. Any other film may be used, but the low-speed, high-contrast film such as process, process panchromatic, commercial, or commercial ortho will be found best for most subjects. If there is a tendency for the uncalcified portions of the bone to acquire a reddish stain, the panchromatic films should be used. In most cases the orthochromatic films are preferable, since development may be carried out in red light.

Development of the film and of the subsequent prints should be carried out according to the manufacturer's directions, although it has been found convenient in this laboratory to use the same developer (Eastman Kodak Formula D 72) for both film and paper.

### Summary

The technic of staining and photographing rat bones for records of vitamin D assays is described. The apparatus and technic employed allow the photographing of as many as 80 single rat radii on a  $12.5 \times 17.5$  cm. ( $5 \times 7$  inch) film at  $2\times$  magnification.

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RECEIVED August 5, 1937. Journal series paper of the New Jersey Agricultural Experiment Station, Department of Agricultural Biochemistry.



ULTRAFILTRATION PROCESS, LILLY RESEARCH LABORATORIES



# Designs for Laboratory Fractionating Columns

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THE perfection and use of small glass rings for packing laboratory fractionating columns as first described by Wilson, Parker, and Laughlin (3) have greatly improved the efficiency and flexibility of laboratory fractionations. In order to make more complete use of this improved efficiency as well as to make it more adaptable for a variety of uses, the following designs for glass columns were devised, and were found satisfactory for the special purposes for which they were made. Their use requires no special equipment nor apparatus not found in any moderately well-equipped laboratory, and their construction from the usual stock sizes of Pyrex glass tubing is relatively easy.

nating the need of grease. A groove, ground on the surface of the plug in the direction of its length and to a depth of about 1 mm., enables the liquid to flow from the condenser to receiver. Adjustment is made by turning the plug from above. A dropping tip on the lower end of the condenser directs the liquid into a

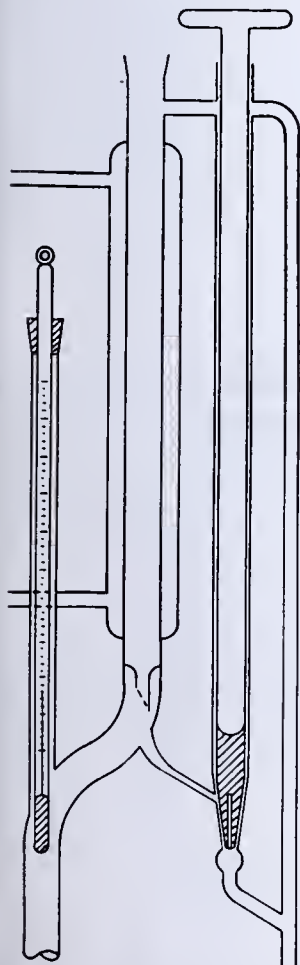


FIGURE 1. LIQUID PARTITION TAKE-OFF

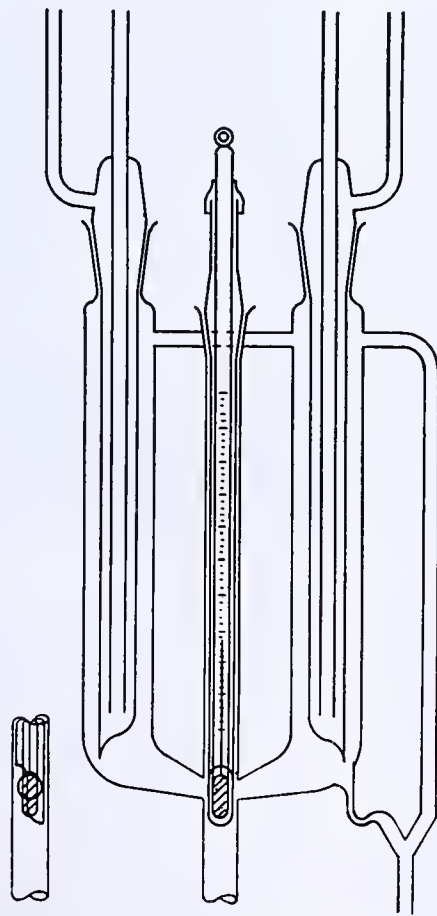


FIGURE 2. VAPOR PARTITION TAKE-OFF

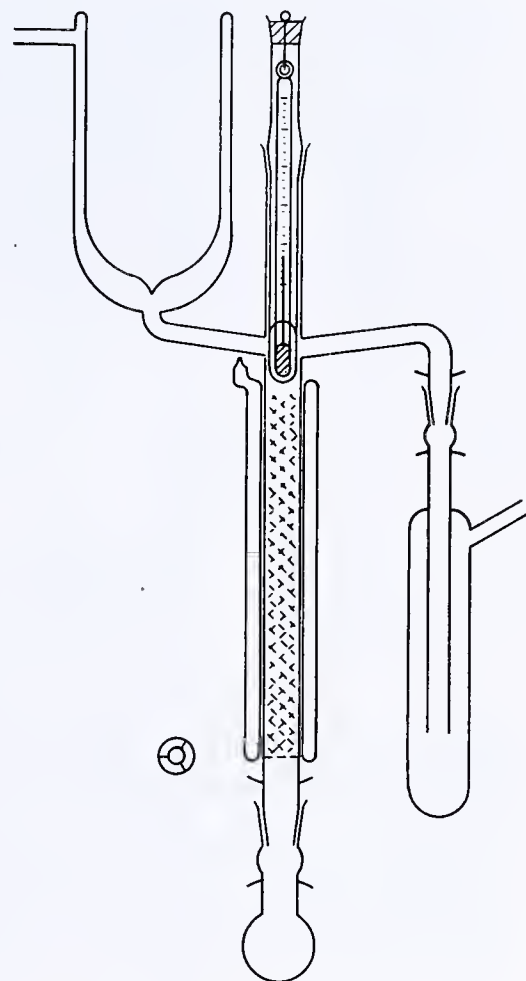


FIGURE 3. COLUMN FOR MODERATELY LOW TEMPERATURES

small cup, which is connected to the plug seat by a piece of capillary tubing. For vacuum distillations and for distillations requiring the exclusion of atmospheric air, a small rubber tubing (not shown in the diagram) placed below the plug handle and over its jacket closes that opening, and the top of the condenser is appropriately closed.

## Vapor Partition Take-off

In Figure 2 is shown a design of the head of a column with a device for partitioning the hot vapor between two condensers, one for reflux and the other for take-off. This design has been found very satisfactory in regard to rigidity of construction, ease of use, and the fineness of adjustment possible. The valve stem is made of a piece of tubing that makes a sliding fit without grinding in its jacket. A ground joint is made with its jacket at the top. The lower end is trimmed off as shown in the side view. The thermometer is hung inside the valve stem.

The take-off trap is made of capillary tubing, and the eccentric dropping tip of the condenser enables the liquid to be directed into a small cup just above the capillary. This cup enters the outside tube slightly, so that it does not receive the liquid condensing on the outer wall. As the partition valve is sealed only with a film of the liquid being distilled, it does not make a complete gas-tight joint. However, if 100 per cent reflux is desired, the take-off condenser can be rotated so that its eccentric dropping tip is not above the receiving cup.

## Liquid Partition Take-off

In Figure 1 is shown a design for the head of a column in which the liquid is partitioned for take-off by means of a ground plug. The liquid condensate itself forms the lubricant, elimi-



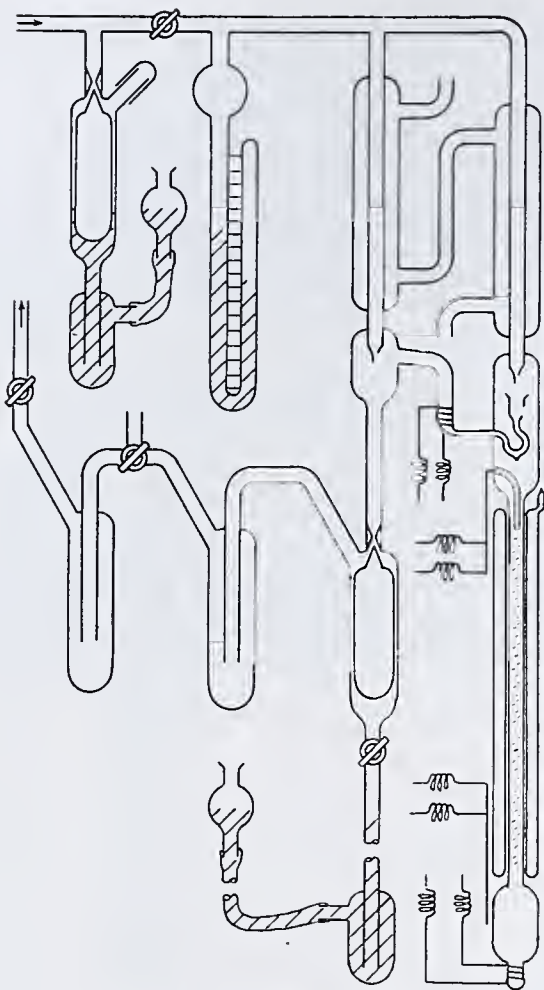


FIGURE 4. PRESSURE COLUMN

The two condenser wells and also the take-off tube are connected with bridges of tubing to equalize the pressure. This design is suitable for vacuum distillations.

### Column for Moderately Low Temperatures

Distillations carried out between about  $-5^{\circ}\text{C}$ . and room temperature offer some difficulties. For this work columns using laboratory water cooling are not suitable and low-temperature columns using liquid air for the condensing medium are expensive to make, difficult to operate, and usually work poorly in this temperature range.

Figure 3 is a diagram of a simple column made to operate in this range. A vapor partition valve similar to the one described above is used. The condenser is a large double-walled vessel in which can be placed ice, ice and salt, or other cooling materials. A nonsilvered vacuum jacket is used to heat-insulate the column proper. A jacket of this construction is only slightly more difficult to make than an ordinary all-glass condenser. The small section of the base of the column shown on the left is the detail of the support for the packing. The small circle with three extending arms is made of thin rod, and it can be easily sealed into the column tube by resting it on a rod of graphite.

When the column is in operation a wide-mouthed laboratory vacuum flask containing the same cooling materials used in the condenser surrounds the receiver. Multiple receivers can of course be used.

### Pressure Column

Distillations at pressures above one atmosphere are desirable for a number of purposes, such as: (1) distillations of mixtures for which rectification at one atmosphere causes little or no separation but for which a better separation can be obtained at higher pressure, because of the change of the phase diagram with pressure; (2) distillation with laboratory water cooling of mixtures normally boiling below room temperatures; and (3) distillation of substances which solidify not far from the normal boiling point.

A diagram of a glass pressure column is shown in Figure 4. As neither stopcocks nor ground-glass joints can be used under pressure, especially when in contact with nonpolar substances being distilled, a method of take-off not depending on their use is employed. The liquid dropping from the end of the reflux condenser is caught in a small cup, which has a hole in its side for the escape of the reflux liquid. A capillary tube connected to the bottom of this cup makes a small trap and then extends through the wall of the column, where it is connected to a larger tube extending upward. Take-off is accomplished and controlled by reboiling the liquid in this larger tube, using a small electric heater made of a winding of Nichrome wire. The reëvaporated material is then condensed in a second condenser.

Air pressure is applied at the top of the column and controlled by an air-filled and sealed glass bulb floating in mercury. This has a ground-in seat at the top, and regulation is obtained by adjusting the height of the mercury leveling bulb. The escaping air exhausts to the atmosphere. A similar device below the take-off condenser enables the condensate to be removed to atmospheric or lower pressure without reducing the pressure on the column. In the design shown, which was used for liquids boiling below room temperature, the condensate evaporates on reaching the low-pressure side of this second regulating valve and is caught in traps. For other purposes and especially for distilling materials that melt close to their normal boiling points, variations of this design would be used, depending upon the properties of the particular substance to be distilled.

Heat is supplied from a winding of resistance wire around a small extension at the base of the pot. Temperatures are determined by thermocouples, one on the side of the pot and the other in a thermocouple well at the top of the column. A nonsilvered vacuum jacket provides heat insulation for the column proper. A closed-tube air-filled manometer is used to determine the pressure. Pressures as high as five atmospheres can be used with safety, provided the tubing is not of extremely large size and the seals are well made.

### Low-Temperature Column

A number of designs for low-temperature columns have previously been described. For example, Rose (2) showed one design and gave a partial bibliography of others. In a recent paper Booth and Bozarth (1) described in detail the construction and operation of a low-temperature column. The one shown in Figure 5 is included here because it has some novel

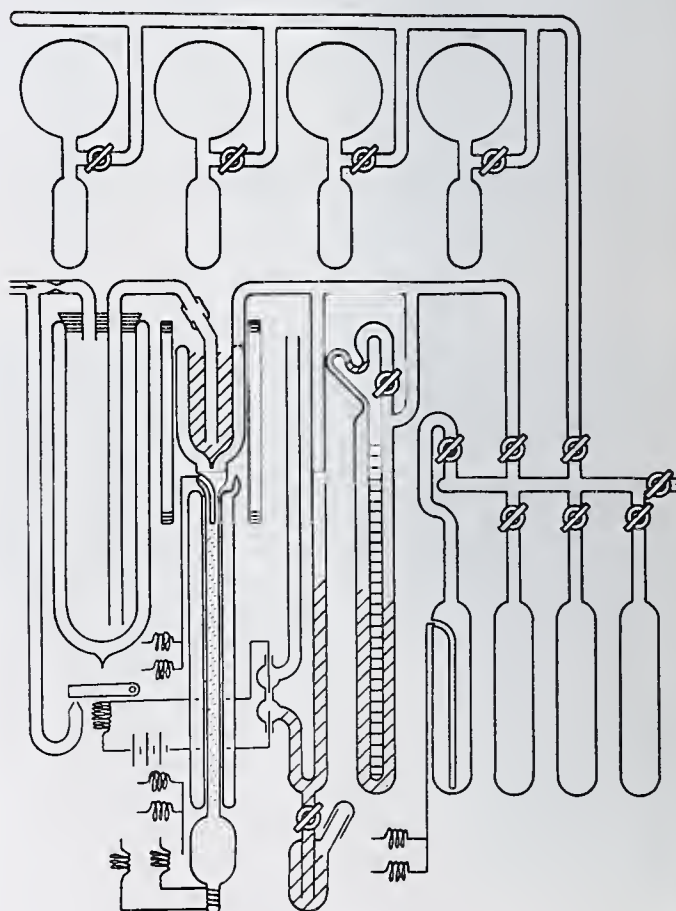


FIGURE 5. LOW-TEMPERATURE COLUMN



features, because it is inexpensive and not too difficult of construction, but chiefly because it has proved very reliable and requires very little attention in operation.

The auxiliary parts of the system, such as receiving bulbs and storage vessels, are also shown in the diagram. The completed system is all-glass and vacuum-tight. It operates as a closed-system partial-condensation column.

The condenser is double-walled. Within the inner tube copper shot and sheet furnish a heat capacity. In this is embedded a copper tube for the admittance of liquid air, which is supplied from a 5-liter container by means of an air pressure siphon. The air is allowed to flow continuously during a distillation, but a by-pass before the liquid air container permits it to escape to the atmosphere. When the pressure in the column rises to a value for which the system has been adjusted, an electrical contact is made in the pressure regulator manometer, and an electrical circuit is closed. This brings the hammer of a relay onto the end of the air escape tube, and liquid air is then forced into the condenser. This lowers the pressure in the column, the electrical contact is broken, and the flow of liquid air stops. By this means distillations can be carried out at any desired pressure from atmospheric down, and the pressure fluctuations during operation are insignificant in regard to the operation of the device for fractional distillations.

The column proper is heat-insulated by a vacuum jacket, which is silvered except for a vertical strip left clear to permit observations of the column. The condenser head is insulated by two concentric glass tubes with an air space between and either silvered or containing a polished metal foil. Tempera-

tures are determined by means of thermocouples, one located in a well at the top of the column and the other on the side of the pot. Heat is supplied by a winding of resistance wire around a small extension on the base of the pot. In operation a cooled wide-mouthed laboratory vacuum flask surrounds the pot. In addition to the regulating manometer an evacuated closed-tube manometer is provided for pressure measurements. Take-off is adjusted by means of stopcocks.

The receiving vessels are arranged in parallel on a manifold. One of these has a thermocouple well in it, and its stopcock is located as shown in the diagram to prevent the accumulation of grease in the bulb. Freezing points and vapor pressures are determined on samples in this vessel, which is surrounded with a heavy-walled copper tube. A vacuum flask is placed around the copper tube, and time-temperature warming curves are taken of the sample. Pressures are determined at the same time. A gas density balance (not shown in the diagram) enables the molecular weight to be simultaneously determined.

The storage vessels are 12-liter flasks provided with condensing bulbs. The material is condensed in the bulb, the stopcock is closed, and the material is allowed to evaporate into the flask.

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RECEIVED September 6, 1937.

## Devices for Extraction by Immiscible Liquids

H. J. WOLLNER AND JOHN R. MATCHETT, U. S. Treasury Department, Washington, D. C.

IN CHEMICAL technology it is frequently necessary to scrub a solution containing one or more solutes, by means of an immiscible solvent.

The efficiency of transferring a dissolved substance from one of two immiscible solvents to the other is a function of the area of contact developed between the two liquids. The development of very large areas of contact usually requires high dispersion of one of the solvents in the other, frequently resulting in stable emulsions. This condition is further aggravated by the desire for maintaining the quantities of extracting liquid as low as possible—usually a fraction of the volume of the original solution.

Where small amounts of the more viscous, solute-bearing phase are intentionally dispersed in large proportions of the less viscous (scrubbing) phase, clean partial separation generally follows when agitation is stopped. However, since it is usually desirable to maintain the extracting phase in smaller volume than the extracted phases, the above condition cannot readily be met in an intermittent process.

The device described below affords rapid and convenient means for maintaining the necessary preponderance of less viscous material, and of making any required number of extractions in a single operation.

The device consists of an emulsification chamber and a settling chamber, connected by two ducts which permit the continuous cycling of the emulsion. Of these two ducts, the first continuously bleeds the emulsified solutions into the settling chamber, where partial separation takes place. That portion which has not clarified is continuously recycled through the second duct back to the emulsification chamber. The clarified extracted solution (previously dispersed phase) is bled off the separating chamber at the same rate at which the unextracted original solution enters the emulsification chamber from a previous reservoir.

Inasmuch as the separation is largely a function of the relative densities of the two liquids and the relative densities of the two phases may vary, it was necessary to design two modifications of the device—one for extracting solvents of lower density than the dispersed phase, and the other vice versa.

### Solute-Bearing Liquids of Greater Density than Extracting Liquid

The emulsification chamber, *A*, is provided with an efficient stirrer, driven by a high-speed motor, and so designed as to lift the solution from the bottom rather than force it down from above. Suitable baffles are provided to ensure thorough mixing of the liquids. The separation chamber, *B*, consists simply of a

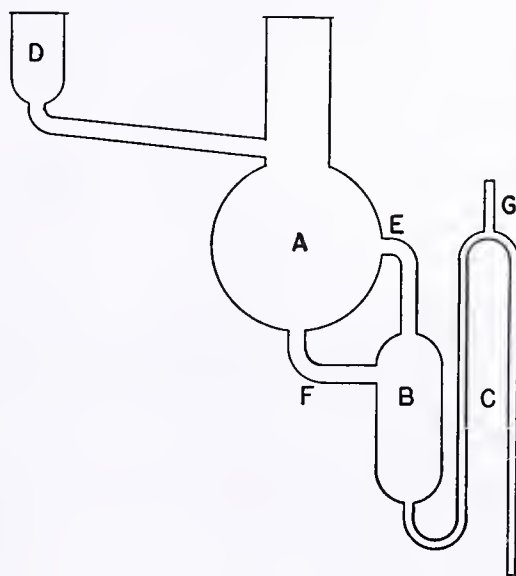


FIGURE 1



tube, the length and bore of which are chosen with respect to the ease of separation of the liquids involved, both dimensions being increased for liquids which do not separate rapidly. Increasing the bore of the tube hastens clean separation, and increasing the length provides added assurance that the partially emulsified interfacial portion will not be withdrawn should the separation, for any reason, momentarily fail to be sharp. On the other hand, it is desirable that the volume of the tube be small in order to retain a minimum of the phase passing through.

The ducts, *E* and *F*, provide a path for the circulation of emulsified material. The mixed liquids pass into the separation chamber through tube *E*. The portion of denser liquid (previously dispersed phase) which separates cleanly remains, and the unclarified balance is drawn back through tube *F* into the emulsification chamber by the action of the stirrer.

The withdrawal tube, *C*, is arranged as indicated in Figure 1. The height of the riser is governed by the relative densities of the phases involved, and by the relative volumes of each present during an operation. The purpose of the open tube, *G*, is to prevent siphoning. By closing the tube the device may be emptied by siphoning. The feed funnel, *D*, may obviously be arranged in any convenient manner.

Dimensions of the apparatus may be chosen with respect to the use to which they are to be put. The following have been found satisfactory: The emulsification chamber, *A*, is a 50-cc. round-bottomed flask, provided with indentations at irregular intervals to act as baffles. The separation chamber, *B*, is made of 22-mm. tubing and is 5 cm. in length. Its top is at the level of the bottom of the flask. The connecting tubes, *E* and *F*, are made of 6-mm. tubing. The withdrawal tube, *C*, is 5-mm. tubing. The head of the riser is 6 mm. above the center of chamber *A*.

### Solute-Bearing Liquids of Lesser Density Than Extracting Liquid

The device is in all respects similar to that shown in Figure 1, except that arrangement is made at *C* for the continuous removal of the upper layer (clarified, extracted, dispersed phase) in the separation chamber, *B* (Figure 2).

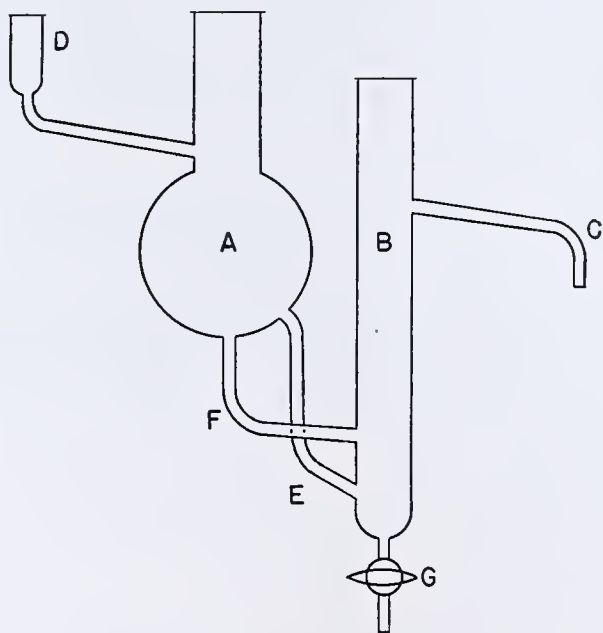


FIGURE 2

Tube *E* crosses tube *F* and enters separation chamber *B* at a point slightly lower. This arrangement is not absolutely essential but tends to allow a more complete withdrawal into the emulsification chamber, *A*, of the unseparated liquid mixture. A stopcock, *G*, is provided for the withdrawal of the contents at the end of the operation.

When the extraction operation is finished an upper layer separates in chamber *A*. By continuing the stirring after all solution has passed in, this layer may be made very small. It is recovered along with that in chamber *B* when the solvent has been withdrawn through stopcock *G*.

The following dimensions have been found suitable: The emulsification chamber, *A*, is a 50-cc. round-bottomed flask,

indented at irregular intervals. The separation chamber, *B*, is made from 22-mm. tubing and is 10 cm. in length from the bottom to the withdrawal tube, *C*. The connecting tubes, *E* and *F*, are of 6-mm. tubing, and are so arranged that tube *E* enters the separation chamber below tube *F*. The withdrawal tube, *C*, is placed just below the height to which the liquid in chamber *A* rises when the stirrer is in operation. A point 3 cm. above the bottom of chamber *A* has been found satisfactory. Stopcock *G* is for draining the apparatus at the completion of a run. The feed funnel, *D*, is arranged in any convenient manner.

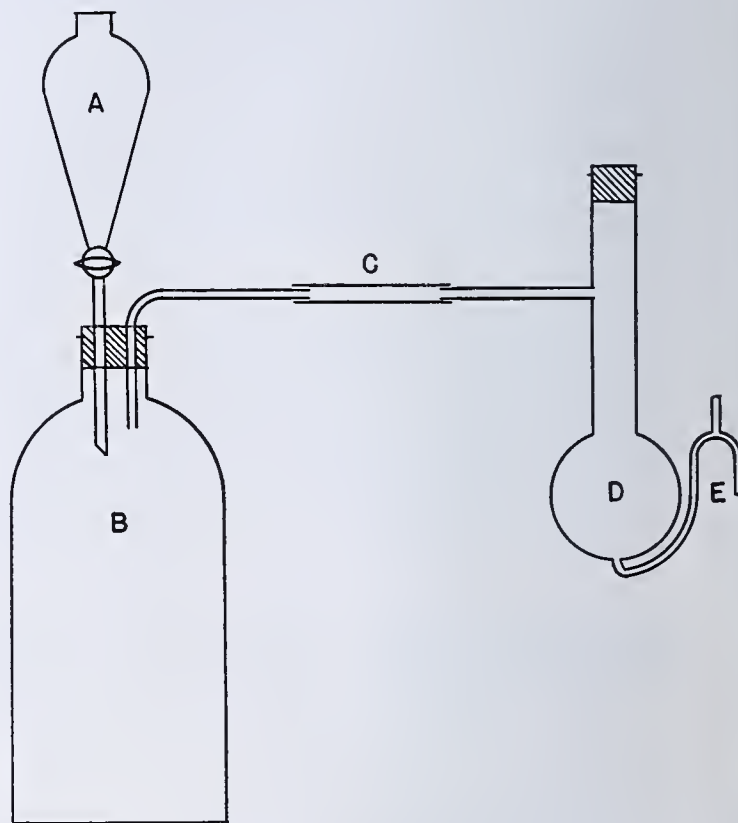


FIGURE 3

For smooth operation the position and speed of the stirrer within chamber *A* must be carefully adjusted, to attain a thorough mixing and rapid circulation of the liquids. A constant rate of flow of feed material must also be assured and this must be so regulated as to maintain a sharp separation of layers in chamber *B*. If these conditions are met the extractors will operate with very little attention.

In order to provide a satisfactory flow of feed material, the device shown in Figure 3 may be used.

Water dripping from the funnel, *A*, into the bottle, *B*, displaces air and forces the feed material from the reservoir, *D*, through the tube, *E*, at a steady rate. Tube *E* rises higher than the liquid level in the reservoir when it is filled and is provided with a vent to avoid siphoning. More precise control may be had by inserting a screw clamp in the rubber connecting tube, *C*.

Any volume of solution may be passed through either extractor. If more than a single extraction is desired the required number may be accomplished in one operation by connecting the necessary number of devices in series. Multiple extraction, with several solvents, can readily be accomplished in a single operation by setting up an equivalent number of these devices in series.

With this device it has been possible to extract 250 ml. of a saliva solution containing 15 gamma of morphine, and recover sufficient morphine to produce an excellent crystal identification.



# The Smoke Tendency Lamp

## Use in Testing Kerosenes

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**D**URING the last 15 years or so considerable attention has been paid by oil refiners to the production of high-grade kerosenes for domestic and foreign markets, the application of improved refining processes being attended by the development of more informative and reproducible laboratory testing procedures. In a previous article (1), the present authors described the improved factor lamp and its use in their laboratories for determining the smoke tendency of various grades of kerosene. It has seemed advisable to redesign the improved factor lamp to embody such features as portability and compactness, and to make a precision instrument capable of at least the same degree of reproducibility.

These efforts have resulted in the development of a new instrument known as the smoke tendency lamp (Figure 1) which is described below.

### The Smoke Tendency Lamp

This instrument consists of the following parts:

**THE FOUNT** is cylindrical in shape, about 1.5 inches in diameter, and 3 inches in height, with closely fitting top carrying wick tube 0.25 inch in diameter. The fount screws into a housing mounted on the horizontal base plate, fine adjustment being obtained by means of the bottom knurled flange. The wick tube is thus raised within a slightly wider outer tube mounted on the base plate.

**THE WICK** is American Pett, 0.25 inch in diameter.

**THE SCREEN** is cylindrical in shape, of 20-mesh brass, 1.5 inches in height, and approximately 1.0 inch in diameter, open at both ends, and is placed concentrically around the outer wick tube on the base plate. This screen allows uniform entrance of air at the base of the flame.

**THE CHIMNEY** is made of heat-resistant, uniform glass tubing, 7 inches long, 1 inch in outside diameter, and 0.03 to 0.06 inch in thickness. The chimney rests on the top of the screen and is held in a vertical position by a side support screwed on to the base plate.

**THE SCALE** is made of Bakelite, black mirrored finish, with white line graduations from 0 to 130 mm., and is mounted vertically on the base plate, the zero mark being on a level with the top of the wick tube.

**THE SPOT PLATE** is mounted on the base plate by means of a vertical rod about 9.5 inches high. It is of porcelain, 1.75 inches in diameter, 0.44 inch in height, and supported horizontally in a ring. The latter is free to move in a horizontal plane by turning the knurled knob at the right of the fount.

**THE LEVEL** is mounted at the front of the base plate.

**THE BASE PLATE SUPPORT** is approximately 8.5 inches in height, semicircular in shape, with round heavy ring base fitted with leveling screws.

**AIR HOLES** are drilled in the base plate in circular fashion around the screen to allow free entry of air through the screen to the flame.

**THE HOOD** is approximately 10.5 inches in height, semicircular in shape, with front glass door, and hinged top containing air holes. It is black inside, and close fitting on base plate.

### Procedure

The sample of kerosene under test is poured into the fount up to the filling mark, and a piece of wick 3.5 inches in length is cut and fitted into the wick tube. The protruding end of the wick is to be clean cut and then burned, so that the rounded tip is only just charred. It should contain no rough edges, and protrude exactly 0.25 inch from the top of the wick tube. The assembled fount is then screwed into place so that on lighting the wick a small flame is obtained. The screen, chimney, and spot plate are placed in position, a small piece of ice is placed on the plate, the hood door and top are closed, and the lamp is set aside for about 15 minutes, preferably in a darkened room, to attain equilibrium conditions.

At the expiration of this period, the flame height is increased by turning the knurled flange of the fount, the spot plate being centered periodically above the chimney by manipulating its control knob below the base plate. A flame height will eventually be reached at which a smoke spot is just formed on the bottom of the spot plate, the flame at this point forming a smoky "tail." The flame is then turned down slightly and again raised until the maximum height is obtained without forming a smoke spot. At this point the flame height is read on the scale, the eye being placed on a level with the extreme luminous tip of the flame. It is convenient to use darkened glasses when viewing the flame. This reading in millimeters is recorded as the smoke tendency of the sample under test. The flame is then turned low and the procedure is repeated at least once, the average smoke tendency value being reported.

TABLE I. TEST RESULTS

Sample	Smoke Tendency Lamp		Improved Factor Lamp	
	Inspector A	Inspector B	Inspector A	
	Mm.	Mm.	Mm.	Inches
Laboratory 1				
A	35, 35	36	39	1.50
B	60, 61	62	66	2.60
C	69, 69	69	76	3.00
D	80, 79	80	83	3.25
Laboratory 2				
A	37	37	37	1.45
B	64	65	66	2.60
C	68	69	74	2.90
D	80	80	86	3.40

### Results

With care and proper attention to details, results on duplicate samples should agree within 2 mm. (0.07874 inch). This degree of reproducibility is obtained only when the equipment is kept in good condition; the screen should be kept free of dust and lint, the chimney clean and polished.

Tests results obtained on four kerosenes, compared with those on the same samples by the improved factor lamp, are given in Table I.

It will be noted that the smoke tendency lamp gives values slightly lower than the improved factor lamp. However, the

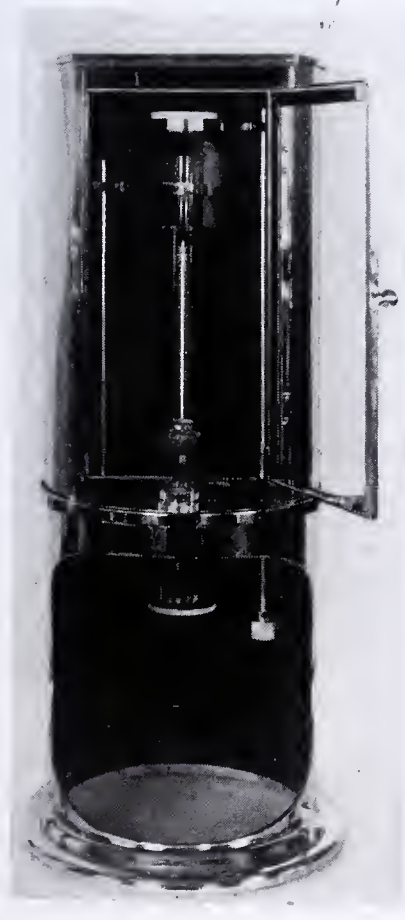


FIGURE 1



various grades of kerosene are rated in the same order and are tested with equal precision.

### Acknowledgment

Acknowledgment is hereby made of the valuable assistance of P. S. Williams of the Manufacturing Engineering Department in developing various mechanical improvements, and

of opinions and comments from members of the Inspection Laboratories at Richmond and El Segundo.

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RECEIVED September 23, 1937.

# Fractionating Device for Vacuum Distillations

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SEVERAL devices have been described for removing fractions of distillate without interrupting the course of a distillation under reduced pressure. Thorne (5) originated an apparatus for this purpose which employed three stopcocks, and many modifications and elaborations have since appeared. Sattler (4) designed an arrangement to eliminate some of the difficulties inherent in the earlier types. A simple device due to Nason (3) is also used, wherein but two stopcocks are required. However, the distillation must be interrupted while the receiving flask is being evacuated, and this is often undesirable. In some modifications the distillate is collected in a receiver having two chambers, one of which can be restored to atmospheric pressure and the fraction of distillate withdrawn without disturbing the vacuum in the other chamber. A compact model of this type employing four stopcocks was worked out by Delaby and Charonnet (2). One of the most convenient of these de-

vices is that designed by Bogert (1) which has a graduated receiver so that fractions of known volume can be collected, and utilizes three stopcocks. In the device to be described the functions of from two to four taps are combined in a single stopcock, which is advantageous in collecting fractions rapidly.

The stopcock plug is hollow, with two 2-mm. tubes sealed in diagonally, in the manner of an ordinary three-way stopcock. Three 3-mm. holes are drilled through the wall at the smaller end of the plug to communicate with outlets *T* and *G*. One hole is drilled in line with the sealed-in bores and communicates with *G* when the plug is in the position illustrated. The other two holes are drilled at an angle of 90° to the first. One of them coincides with outlet *T* when the plug is in the position shown; the other is directly opposite. Tube *T* enters the shell of the stopcock at the rear and at a right angle to the plane of the drawing. The upper end of this tube enters the upper part of the receiver near the connection for the condenser. The condenser tube should be so arranged that liquid cannot enter tube *T*. Tube *L* is bent to the rear and the end expanded for rubber tubing connection.

The receiver is attached to the condenser at *A*, a receiving flask is placed at *B*, and the pump is connected at *C*. The stopcock is then turned to the position shown. The entire system can be evacuated, since ports in the hollow plug communicate with *T* and *G*. The distillation is allowed to proceed, and when it is desired to collect another fraction the stopcock is turned 180°, whereupon air or an inert gas is admitted through tube *L* to the receiving flask. The distillation continues into receiver *R*, the vacuum being maintained through tube *T* and the port in the hollow stopcock. A new receiving flask is placed at *B*, and upon turning the stopcock 90° in the proper direction the receiving flask will be evacuated through tube *G*, while the rest of the system is momentarily disconnected from the pump. The stopcock is then turned 90° farther and the original position is resumed, the accumulated distillate running into the receiving flask. The receiver, *R*, may be graduated if desired.

It is impossible to let air into the system accidentally in excess of the amount contained in the receiving flask if the latter is in place. This is also true of the apparatus as originally designed by Bogert, but unfortunately in many modifications which have appeared this provision has been neglected. In some designs the connection for an inert gas is through a stopcock with a "tail" plug, and the tension of the rubber tubing may push it out. In the device described this is avoided and the plug is held in place by atmospheric pressure. Because of the compact construction the device is not as fragile as it might appear.

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RECEIVED October 4, 1937.

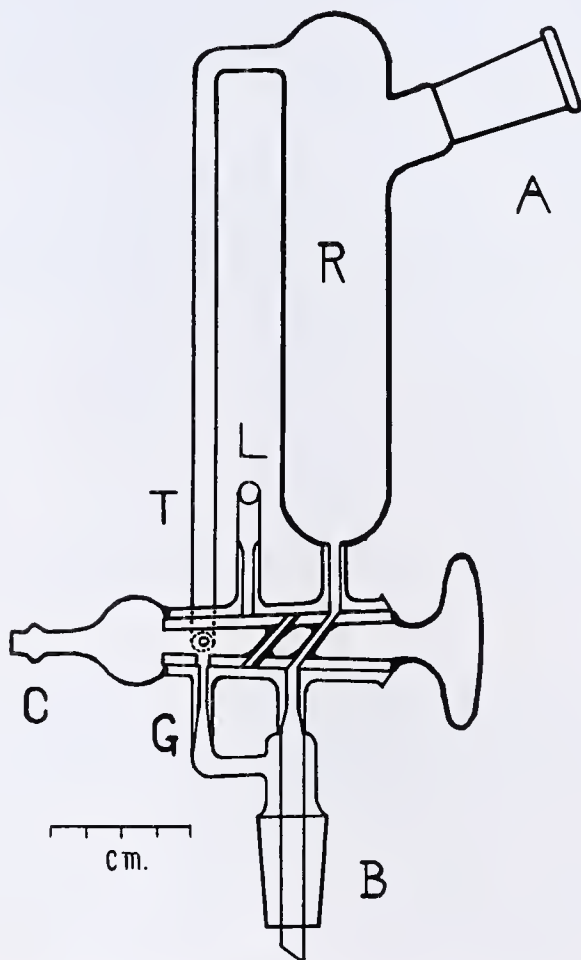


FIGURE 1. DIAGRAM OF APPARATUS



# A New Capillary-Type Viscometer

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THE fact that several new types of viscometers have of late years appeared for determining viscosity in absolute measure as substitutes for the conventional viscometers of the Engler, Redwood, and Saybolt types seems to indicate that certain difficulties are experienced in procuring a viscometer for this purpose which is well suited for practical use. The transition from the use of technical viscosity units to the use of absolute units gives rise to difficulties in practical life, the more so because the comprehension of the viscosity conception and of the sources of the errors which may occur in the determination of viscosity in absolute measure, demands a knowledge of physics which is not required in dealing with empirical viscosity conceptions.

In the recent literature an account has been given of the advantages and disadvantages of different types of viscometers (5).

The requirements which a standard apparatus must fulfill are as follows:

The viscometer must be of simple construction and cheap to manufacture.

The quantity of testing liquid necessary for determining the viscosity must be small.

The apparatus must have a wide viscosity determination range.

Different capillary actions of liquids must not give rise to errors in the determination. When this requirement is fulfilled, it is possible not only to carry out the calibration of the apparatus with liquids having a surface tension different from that for which the viscometer is generally to be used, but also to avoid errors in the viscosity determinations at different temperatures caused by the fact that the surface tension of the liquids varies with the temperature.

It must be possible to make the zero adjustment and to carry out the measurement of volume with great accuracy.

It must be possible to make the temperature measurement directly in the liquid under test, and to determine the viscosity over a wide range of temperature (also at temperatures far above 100°C.).

In designing the present viscometer, an effort has been made to fill these requirements. Further, it is possible with a special construction of the viscometer to determine the surface tension of liquids.

A short account of the theoretical basis of the viscosity determination in absolute measure is given below, followed by a description of the viscometer, an account of the manner in which it is employed, and comments illustrating its applicability and the accuracy which may be expected in use.

## Theoretical Basis for Determination of Kinematic Viscosity

Flow of liquids at low speed through capillary tubes takes place in parallel tracks, the speed increasing from 0 at the tube wall to a maximum in the axis of the tube (laminar flow). For laminar flow in capillary tubes, Poiseuille's formula modified by Hagenbach and Couette applies.

$$\eta = \frac{\pi \times p \times r^4}{8 \times V \times l} \times t - \frac{m \times \rho \times V}{8 \times \pi \times l} \times \frac{1}{t} \quad (1)$$

where  $p$  = head which causes the outflow of the liquid  
 $l$  = length of the capillary tube  
 $V$  = efflux quantity  
 $r$  = radius of the capillary tube  
 $\rho$  = density of the liquid  
 $t$  = efflux time  
 $\eta$  = dynamic viscosity of the liquid  
 $m$  = a calibration constant

The last factor expresses a correction for that part of the pressure energy which is spent in increasing the kinetic energy during the influx of the liquid into the capillary tube.

If the driving pressure is caused by the liquid sinking from a higher level to a lower one, then

$$p = g \times \rho \times h \quad (2)$$

where  $g$  = gravity acceleration, and  $h$  = the mean head

If Equation 2 is introduced into 1, then

$$\eta = \frac{\pi \times g \times h \times r^4}{8 \times V \times l} \times \rho \times t - \frac{m \times V}{8 \times \pi \times l} \times \rho \times \frac{1}{t} \quad (3)$$

For the same apparatus, all values with the exception of  $\eta$ ,  $\rho$ , and  $t$  are constant, wherefore

$$\eta = k \times \rho \times t - K \times \rho \times \frac{1}{t} \quad (4)$$

where  $k$  and  $K$  are calibration constants

If  $\nu = \eta : \rho$  is introduced into Equation 4, then

$$\nu = k \times t - K \times \frac{1}{t} \quad (5)$$

or

$$\nu = k \times \left( t - \frac{K}{k \times t} \right) \quad (6)$$

The last factor in Equation 6 denotes the number of seconds by which the efflux time is to be corrected when alterations in the kinetic energy are to be considered during the efflux—a correction which is of no importance at slow outflow.

If this correction is disregarded, then

$$\nu = k \times t$$

The constant  $k$  is determined by measuring the efflux time,  $t$ , for a calibration liquid with known kinematic viscosity,  $\nu_1$ , from

$$k = \frac{\nu_1}{t_1} \quad (7)$$

With this  $k$  value, the kinematic viscosity,  $\nu$ , of a certain liquid is determined by the formula

$$\nu = k \times t \quad (8)$$

where  $t$  is the efflux time at the measuring temperature.

## Method of Viscosity Determination

TESTING APPARATUS. The viscometer, which is shown in Figure 1, permits viscosity determinations over a wide range, and is designed with a view to reducing to a minimum deviation originating from the difference in the capillary action of liquids.

After the viscometer had been tested with good results in a series of industrial laboratories, it was accepted by the Danish Standardizing Council as standard apparatus for examining the viscosity of technical oils.

The viscometer is U-shaped. One side is a wide glass tube; the other side, the capillary side, is divided by the bulb into an upper tube and a lower capillary tube.

The wide tube has an annular red mark,  $a$ , at the bottom and millimeter division downwards as shown. A thermometer, the mercury of which bulb has the same diameter (7.5 mm.) as the stem, is placed axially in the tube, sliding in a cork stopper with lateral slit. The thermometer serves partly to measure the temperature of the sample and partly to adjust the heights of liquid before the measurement commences.



The capillary tube has a white mark, I, and two blue marks, II and III. Just below and above bulb A, two red marks, IV and V, are placed.

It is practical to place the viscometer in a metal stand (Figure 2), by which it is protected against breakage. The capillary tube side is connected to a suction device. Near the suction device, a three-way cock is inserted to make a connection between the viscometer and the atmosphere and also between the viscometer and the suction device.

**PROCEDURE.** The viscometer may be employed in two ways according to whether the oil sample is thin ( $\nu$  from about 1.5 to 100 centistokes), or viscous ( $\nu$  from about 100 to 5000 centistokes).

A. The viscosity of liquids of comparatively low viscosity is determined by introducing the sample into the viscometer until the liquid surface in the wide tube is about 5 mm. below mark *a*. Then the stopper with the thermometer is placed in the wide tube, and the viscometer is placed in a liquid bath of the temperature at which the viscosity is to be determined, so that the mark, V, on the capillary tube side is a little below the surface of the bath.

When the sample has assumed the testing temperature, the liquid surface in the wide tube is adjusted to mark *a* by means of the thermometer. If only transparent liquids have to be dealt with, the zero adjustment may be carried out by adjusting the meniscus of the liquid on a level with mark *a*, which in this case also has to be done when determining the viscosity constant

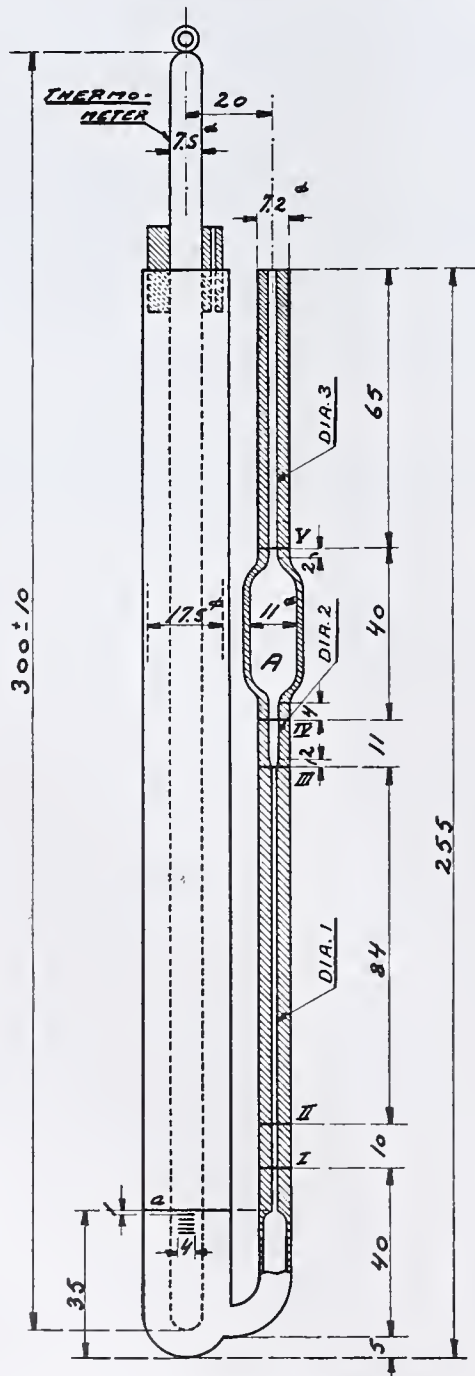


FIGURE 1. DIAGRAM OF VISCOMETER

$k_A$ . The use of the upper surface of the liquid when carrying out the zero adjustment is proposed because this method may be employed with opaque as well as with transparent liquids.

Then the sample is sucked up into the capillary tube side until the liquid surface is a couple of millimeters above mark V, when the three-way cock is opened to the atmosphere, and the efflux

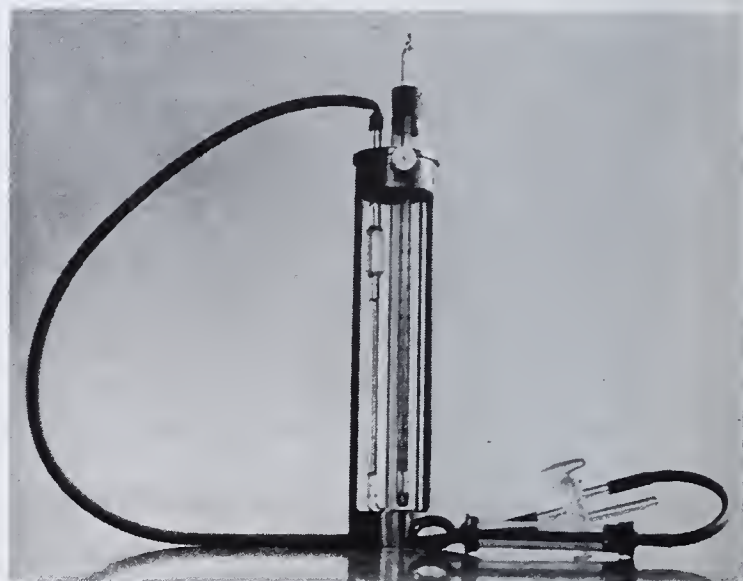


FIGURE 2. VISCOMETER

time of the liquid from mark V to mark IV (the red marks) is determined by means of a stop watch. As a certain time is required to arrive at equilibrium at the boundary surface between the liquid and the viscometer, it will as a rule be found that the first determination of the efflux time differs slightly from later measurements. If the capillary tube side of the viscometer is dry before the test, the liquid should therefore be sucked up to the highest level once and again lowered, before the measurement is made.

The kinematic viscosity of the sample at the measuring temperature is then

$$\nu = k_A \times t$$

where  $k_A$  is the calibration constant which has previously been determined according to the above method with a liquid of known kinematic viscosity, the second factor in Equation 5 being disregarded.

As the capillary action in the bulb is the same as in the wide tube with the thermometer, the influence of the capillary forces on the result is eliminated during practically the entire efflux time.

The question of correction for alteration of the kinetic energy during the outflow is treated below.

B. The viscosity of liquids with relatively high viscosity is determined by introducing the sample into the viscometer as described above, at the test temperature. The liquid surface is adjusted by means of the thermometer so that the meniscus, when the liquid column falls, will settle at mark I on the capillary. The liquid is then sucked up into the lower capillary tube until the surface is a couple of millimeters above mark III, the three-way cock is opened to the atmosphere, and the efflux time from mark III to mark II (the blue marks) is determined.

The kinematic viscosity of the sample at the measuring temperature is then

$$\nu = k_B \times t$$

where  $k_B$  is the calibration constant which has been determined according to the method mentioned with a liquid of known kinematic viscosity, the second factor in Equation 5 being disregarded.

By this method, the influence of the capillary action on the result is eliminated by starting with a suspended level at mark I before the test is commenced, the capillary action during the efflux time being uniform.

The author has previously proposed the use of a single capillary tube with three marks placed at similar distances from each other, as are marks I, II, and III in Figure 1, for the determination of the viscosity of comparatively viscous



TABLE I. DETERMINATION OF CORRECTION

Meniscus	First Series of Tests					Second Series of Tests					Mean	
	Glycerol		Water			Glycerol		Water			$K$	$m$
	$t$	$k$	$t^a$ Sec.	$K$	$m$	$t$	$k$	$t^a$ Sec.	$K$	$m$		
a	117.8	0.1079	10.0	0.716	0.86	117.5	0.1082	10.0	0.746	0.90	..	..
b	152.9	0.0831	13.0	0.950	1.14	151.6	0.0838	13.0	0.971	1.16	0.87	1.03
c	178.4	0.0712	15.0	0.918	1.10	178.4	0.0724	15.0	0.918	1.10	..	..
d	246.4	0.0516	20.2	0.86	1.03 <sup>b</sup>	243.1	0.0523	..	..	..	..	..

<sup>a</sup> Mean values of at least 10 measurements.

<sup>b</sup> Mean values of 5 tests made independent of each other, in each of which the efflux times for water are mean values of 10 measurements, and the efflux times for glycerol for determining the  $k$ -values are mean figures of at least 5 measurements.

liquids, the zero adjustment being carried out by adjusting the capillary tube in a liquid surface until the meniscus in the capillary tube was level with the lowest mark, and the determination otherwise made as mentioned above (3).

**ACCURACY OF DETERMINATION.** The accuracy of the determination is mainly dependent on the degree of accuracy of the temperature measurement, and for a lubricating oil with kinematic viscosity of about 150 centistokes amounts to 1 per cent for 0.1° variation of the temperature at 20° C.

**REFERENCE OIL.**  $k_A$  and  $k_B$  are determined with a mineral oil having a  $\nu$  of about 150 centistokes at 20° C., whose viscosity is accurately determined by the National Physical Laboratory, Teddington, England.

### Correction for Alteration of Kinetic Energy during Efflux

In the foregoing, only the first factor in the Poiseuille-Hagenbach-Couette formula (Equation 1) has been considered. This is permissible in the case of efflux times of more than 40 seconds by which the correction on the efflux time—i. e., the quantity  $\frac{K}{k \times t}$  (Equation 6)—amounts to less than 0.2 second.

**CORRECTION REQUIRED WHEN USING THE BULB PORTION, METHOD A.** The quantity  $K = \frac{m \times V}{8 \times \pi \times l}$  (Equations 1 and 4) may be determined in different ways. A method is described below which does not require the use of other viscometers.

As the wide tube is cylindrical, the correction for alteration of speed during efflux when the bulb portion is used will not be dependent on the place at the cylindrical tube which is chosen as meniscus, but only on the efflux time from mark V to mark IV. For determining the correction, and for obtaining check determinations at different efflux times, the following procedure may therefore be employed:

Above the mark,  $a$ , on the wide cylindrical tube of a viscometer, three marks,  $b$ ,  $c$ , and  $d$ , were placed at suitable distances from each other. Then a determination with glycerol of known kinematic viscosity at 20° C., with use of the bulb portion and with the four marks  $a$ ,  $b$ ,  $c$ , and  $d$  as meniscus, of the  $k$ -values of Equation 7 was made regardless of the alteration of kinetic energy; these  $k$ -values may be called  $k_a$ ,  $k_b$ ,  $k_c$ , and  $k_d$ .

Then the efflux times for water at 20° C. were determined, using the bulb portion and the same four marks,  $a$ ,  $b$ ,  $c$ , and  $d$ , as meniscus. Let us call these efflux times  $t_a$ ,  $t_b$ ,  $t_c$ , and  $t_d$  seconds.

As the kinematic viscosity of water at 20° C. is  $\frac{1.0054}{0.998} = 1.0074$  centistokes, four equations are available, from each of which  $K$  may be determined:

$$\begin{aligned} 1.0074 &= k_a \times t_a - \frac{K}{t_a} \\ 1.0074 &= k_b \times t_b - \frac{K}{t_b} \\ 1.0074 &= k_c \times t_c - \frac{K}{t_c} \\ 1.0074 &= k_d \times t_d - \frac{K}{t_d} \end{aligned}$$

The results are shown in Table I. Glycerol with a specific gravity of 20°/4° 1.16585—25°/25° 1.16648;  $\nu = 12.71$  centistokes is employed.

By measuring out the viscometer employed for these tests,  $V$  was found equal to 2.5538 ml., and  $l = 12.2$  cm. With these values, the values for  $m$  indicated in the table were found from

$$m = \frac{K \times \pi \times 8 \times l}{V}$$

The correction factor  $\frac{K}{k \times t}$  may now

be calculated with an accuracy sufficient for practical purposes.

For  $V = 2.5$  ml.,  $l = 12$  cm., and  $k = 0.1$  the corresponding values for efflux time and correction given in Table II are obtained.

TABLE II. EFFLUX TIME AND CORRECTION

Efflux Time Sec.	Correction, $\frac{K}{k \times t}$
5	1.7
10	0.9
15	0.6
20	0.4
25	0.3
30	0.3
From 35 to 55	0.2
From 60 to 160	0.1

**CORRECTION REQUIRED WHEN USING THE CAPILLARY PORTION, METHOD B.** As by determination of the efflux time from mark III to mark II,  $V$  is a very slight quantity and  $l$  has an appreciable value, and assuming that the value of  $m$  is about 1,  $K$  will be so small that, when using the capillary portion, a correction may be disregarded.

### Correction for Afterflow (Drainage)

Errors will occur in the viscosity measurements if the quantities of liquid which by adhesion are retained on the walls of the glass are different.

When the bulb portion is used, the adhesion is of no importance in proportion to the comparatively large volume of liquids (2.5 ml.).

When the capillary portion is used, the quantity of liquid retained by adhesion is comparatively large in proportion to the efflux quantity, and it was necessary to consider whether this effect causes errors in the determinations. For this purpose, tests were carried out with a capillary tube with discharge cock melted on, and with the same diameter as that of the viscometer, and with corresponding marks.

By an examination of the volume of afterflow, the efflux times for different liquids were determined in the usual man-

TABLE III. CORRECTION FOR AFTERFLOW

Liquid	Efflux Time Sec.	Afterflow, Per Cent of Efflux Quantity
Calibration oil	21.4	11 and 11
White oil	42	12 and 12
Castor oil	160	12 and 12

TABLE IV. CORRECTION FOR AFTERFLOW

Liquid	Efflux Time Sec.	Afterflow, Per Cent of Capillary Volume
Castor oil	322	10.5
Reference oil	47	11.4
Glycerol IV	15	10.5
Oil mixture	4.6	10.6



TABLE V. DETERMINATION OF VISCOSITY CONSTANTS

	Reference Oil <sup>a</sup>			Glycerol <sup>b</sup>			Percentage Difference <sup>c</sup>		
	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>	<i>k</i>	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>	<i>k</i>	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>	<i>k</i>
Raaschou viscometer	0.1266	2.764	....	0.1278	2.761	....	0.93	-0.11	...
	0.1272	2.790	....	0.1285	2.794	....	1.02	0.14	...
Ubbelohde viscometer	....	....	0.1010	....	....	0.1025	..	....	1.5

<sup>a</sup> 150.1 centistokes, 20° C., determined by National Physical Laboratories, Teddington, England.  
<sup>b</sup> 49.73 centistokes, 20° C., calculated by means of Sheely's Tables.  
<sup>c</sup>  $\frac{k_{glyc.} - k_{ref.}}{k_{ref.}} \times 100$ .

ner, whereupon the capillary tube was placed in a thermostat at 20° C. until the height of liquid stopped increasing, and the afterflow was measured.

In Table III, the results of tests made with oils of different viscosities are stated, the afterflow being expressed in per cent of the efflux volume.

By another test with another capillary tube with cock melted on, the afterflow was determined by weighing. The volume between mark III and mark II was determined with water by weighing. During the weighing, the efflux point was covered with a glass cap fastened by means of a rubber ring, to prevent evaporation.

The capillary tube was weighed with four different liquids, before and after the efflux, the levels of the liquids standing at marks III and II, respectively. The difference between two corresponding weighings with the same liquid divided by the specific gravity of that liquid is the efflux volume. The difference between the volume between marks III and II and the efflux volumes is the "afterflows" for the liquids employed, which in Table IV are expressed in per cent of the capillary volume between marks III and II.

The tables show that an afterflow effect will hardly cause an error in the viscosity measurements greater than about 1 per cent.

Determination of Viscosity Constants

For the determinations, the following liquids were used: *glycerol*: Merck, specific gravity 20° C./4° C., 1.20794, viscosity 49.73 centistokes/20° C.; *reference oil*: specific gravity 20° C./4° C. 0.8948, viscosity 150.1 centistokes/20° C.

‡ The kinematic viscosity of the glycerol solution is derived from Table VI in "Glycerol Viscosity Tables" (4): which val-

ues are determined with Bingham's viscometer (1). The specific gravity of the glycerol was determined at 25° C./25° C. and 20° C./4° C., so that the figures of the table which apply for specific gravity 25° C./25° C. may be employed.

The viscosity of the reference oil was determined by the National Physical Laboratory, Teddington, England.

For purposes of comparison, the constant for an Ubbelohde viscometer with suspended level was determined. The results are given in Table V.

The deviations in the *k*-values when determined with reference oil and with glycerol are below approximately 1 per cent when using both the bulb portion (method A) and the capillary portion (method B).

Practical Results

Under the auspices of the Standardizing Council, an examination was carried out as regards the accuracy which may in practice be expected by use of the new standard.

Seven laboratories (I to VII in Tables VI and VII), of which laboratories III to VII had not used the viscometer before, received: 1 viscometer and 3 calibrated thermometers with 0.1° C. graduation at 20°, 50°, and 100° C., respectively; 1 sample of reference oil with kinematic viscosity 150.1 centistokes/20° C. determined by the National Physical Laboratory, Teddington, England; 1 sample of oil marked "xxx Spindle," 1 sample of oil marked "406 oil," 1 sample of oil marked "900 pale," together with a copy of the Danish standard regarding determination of viscosity.

The laboratories were requested to determine the calibration constants, *k*<sub>A</sub> and *k*<sub>B</sub>, and the viscosity of the oil samples at 20°, 50°, and 100° C. according to methods A and B mentioned in the standard, these being applied to an extent suitable for the purpose. The results appear in Tables VI and VII.

Further, laboratory V determined the viscosity of the oils with the Vogel-Ossag viscometer. By means of this apparatus, the viscosity of the reference oil was found to be 150.9 centistokes/20° C.; the viscosities of the other oil samples appear in Table VII.

TABLE VI. DETERMINATION OF CALIBRATION CONSTANTS

Laboratory	Viscometer 1		Viscometer 2		Viscometer 3		Viscometer 4		Viscometer 5		Viscometer 6	
	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>	<i>k</i> <sub>A</sub>	<i>k</i> <sub>B</sub>
I	0.1329	3.167	0.1316	3.076	0.1420	3.070	0.1457	3.089	0.1405	3.134	0.1399	3.044
II	0.1342	3.130	....	....	....	....	....	....	....	....	....	....
III	....	....	0.1324	3.076	....	....	....	....	....	....	....	....
IV	....	....	....	....	0.143	3.07	....	....	....	....	....	....
V	....	....	....	....	....	....	0.147	3.054	....	....	....	....
VI	....	....	....	....	....	....	....	....	0.1395	3.22	....	....
	....	....	....	....	....	....	....	....	0.1400	3.153	....	....
VII	....	....	....	....	....	....	....	....	....	....	....	....

TABLE VII. DETERMINATION OF KINEMATIC VISCOSITY

Laboratory	xxx Spindle						406 Oil						900 Pale					
	20° C.		50° C.		100° C.		20° C.		50° C.		100° C.		20° C.		50° C.		100° C.	
	A <sup>a</sup>	B <sup>b</sup>	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
I	102.2	103.2	23.14	23.02	5.42	..	395.0	396.8	58.54	58.66	9.52	9.35	772.2	772.7	91.60	91.73	12.15	11.94
II	103.2	103.3	23.07	...	5.49	..	...	398.1	58.0	57.8	9.50	..	...	772.0	...	90.0	12.20	11.77
III	103.1	103.7	23.2	23.4	5.40	..	...	399.9	58.9	58.8	9.57	..	...	777.3	91.8	92.3	11.9	...
IV	102.6	103.0	23.01	23.12	5.45	..	...	401.3	58.16	57.99	9.42	..	...	783.2	91.99	92.07	12.18	11.88
V	103.0	103.7	23.3	23.2	5.44	..	...	390.0	58.5	58.1	9.37	..	...	796.0	93.5	91.7	12.16	...
VI	103.5	...	23.15	...	5.47	..	397.0	...	58.4	...	9.35	..	...	...	91.1	...	12.2	...
	103.7	104.1	23.31	23.02	...	..	399.0	402.0	58.45	58.49	...	..	...	782.0	91.9	89.9	...	...
VII	102.5	102.5	23.5	...	...	..	...	391.0	59.4	...	...	..	...	770.0	92.6	...	...	...
Vogel-Ossag viscometer	....	....	23.1	...	6.00	...	399.0	...	58.6	...	9.45	...	804.0	...	93.3	...	....	....

<sup>a</sup> Efflux time by method A for viscosity = 100 centistokes about 750 seconds.  
<sup>b</sup> Efflux time by method B for viscosity = 100 centistokes, about 32 seconds.



Measuring Surface Tension with Viscometer

The viscometer may be used for measuring the surface tension of liquids by measurement of the height to which the capillary column rises when a millimeter scale, the lowest mark of which is level with mark *a* on the wide tube as shown in Figure 3, is cut into the capillary tube. The measurement is carried out by pouring the liquid into the viscometer and adjusting it by pushing the thermometer so that the meniscus is level with mark *a*. The rise of the liquid in the capillary tube is measured, and the surface tension is calculated in proportion to that of reference liquids with known surface tension.

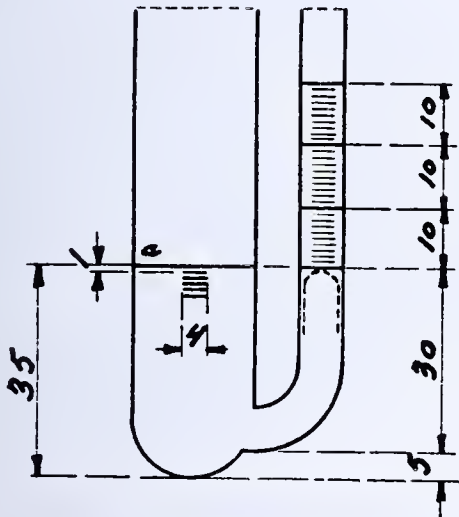


FIGURE 3

From the following series of tests, the accuracy of the method may be judged. The height to which water rises, determined at 18° C., was 27.0 mm. Based on this figure, and on the values stated by Landolt-Börnstein (2), for the specific cohesion *a*<sup>2</sup>, where *a*<sup>2</sup> = *r* × *h*, *r* being the radius of the capillary tube, and *h* the capillary rise, the capillary rises were calculated for a series of liquids (Table VIII).

TABLE VIII. CAPILLARY RISES

Substance	<i>t</i> °	<i>a</i> <sup>2</sup> Sq. mm.	Rise Calculated Mm.	Rise Found Mm.	<i>α</i> from Landolt- Börnstein Dyn./cm.
Water	18	14.878	..	27.0	72.82
Glycerol, sp. gr. 1.228/15°	18	10.71	19.5	19.8	64.67
Aniline	17.5	8.78	15.9	15.8	44.1
Benzene	17.5	6.734	12.2	12.3	29.16

Further, the rise of each of these fluids was determined experimentally with the same viscometer. The values found are stated in the next to the last column of the table. The rises were read without the use of a cathetometer. In the last column, the surface tensions of the liquids in question according to Landolt-Börnstein are given.

The surface tension of a liquid is determined by means of the value, *a*<sup>2</sup> = 14.878, and the rise, 27.0 mm., found for water at 18° C. From this, *r* is calculated which, multiplied by the rise of the liquid concerned, gives the specific cohesion, *a*<sup>2</sup>, for this fluid.

This value introduced into an equation

$$\alpha = \frac{a^2 \times (\rho - \rho') \times g}{2}$$

where *ρ* and *ρ'* are the specific gravities of the liquid and the air, respectively, and *g* = 981.4 cm. per second, gives the surface tension, *α*, of the liquid concerned.

In Table IX, some results of tests are stated; in the calculations, the factor *ρ'* has been disregarded.

This method of measuring surface tension is subject to a slight error, as a small capillary rise, about 1 mm. in the wide tube between the thermometer and the wall of the tube, appears at the zero adjustment. This error is compensated for by employing the rise found for water, and not the rise which is caused by the capillary action = 0 in the wide tube, when calculating the *α* values.

TABLE IX. RESULTS OF TESTS

Liquid	Rise <i>t</i> °	Mm.	<i>a</i> <sup>2</sup> Calculated Sq. mm.	<i>α</i> Calculated Dyn./cm.
Calibration Oil No. 3, sp. gr. 0.8908, 20°/4°	20	13.8	7.60	33.2
Glycerol I, sp. gr. 1.16585, 20°/4°	20	21.8	12.01	68.7
Glycerol II, sp. gr. 1.121403, 20°/4°	20	20.6	11.35	62.5
Saccharose, sp. gr. 1.28555, 25°/4°	25	23.0	12.67	80.0

If a cathetometer is not used for measuring the rise, the error will be negligible as compared with the uncertainty of the readings.

Summary

Tests during the past 3 years in several Danish laboratories have proved that the viscometer described here fulfills the requirements for standard apparatus. It is of simple construction, cheap to manufacture, and requires but a small quantity of testing material. The apparatus has a wide range, as by two different methods it can be used for determining viscosities from about 1.5 to 100 centistokes, and from about 100 to 5000 centistokes. The viscometer is designed with a view to reducing to a minimum deviations originating from the difference in the capillary action of liquids. Not only can the calibration be carried out with liquids having a surface tension different from that for which the viscometer is generally to be employed, but also errors in viscosity determinations at different temperatures, caused by the fact that the surface tension of the liquids varies with the temperature, are reduced to a minimum. The zero adjustment of the apparatus may be made with great accuracy, the efflux quantity is constant, the temperature measurement is made directly in the liquid under test, and the viscosity determinations may be made over a wide range of temperature. Further, the apparatus can be handled easily and quickly.

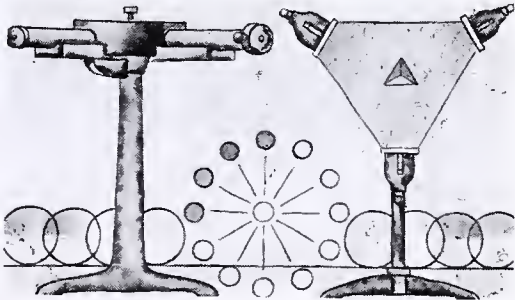
Acknowledgment

In working out this method for determining viscosities, the author has benefited by the help of the members of the committee which prepared the Danish standard for the determination of viscosity, as well as by the help of assistants in his laboratory. He wishes to extend his best thanks to each.

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(2) Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., p. 198, Berlin, Julius Springer, 1923.  
(3) Raaschou, P. E., *Dansk Tids. Farm.*, **2**, 134 (1928).  
(4) Sheely, M. L., *IND. ENG. CHEM.*, **24**, 1060 (1932).  
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RECEIVED July 28, 1937.





# A Method of Preparing Thin Films

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A MODIFICATION of the method recently described by Sager (1) for the preparation of thin films has been used in this laboratory for some time, and is applicable to the spreading of aqueous or nonaqueous dispersions of film-forming materials upon a variety of sheet materials. The dried films from most aqueous dispersions may be readily peeled

Shims of suitable thickness are most conveniently selected by trial and error; a starting point may be arrived at by calculating the thickness of the liquid film which it is desired to apply, and then selecting sheets of paper having suitable caliper.

For reproducible results, the following requirements must be met:

1. The bed plate and the bottom of the spreader bar must be ground in so that, when shims are inserted, the slit between them is of uniform thickness.
2. Durable shims must be provided. Steel feeler gage stock of precise thickness may be obtained from the Starrett Company, Athol, Mass.
3. The viscosity and solids content of the film-forming dispersions must be controlled.

## Literature Cited

(1) Sager, T. P., *IND. ENG. CHEM., Anal. Ed.*, 9, 156 (1937).

RECEIVED September 18, 1937.

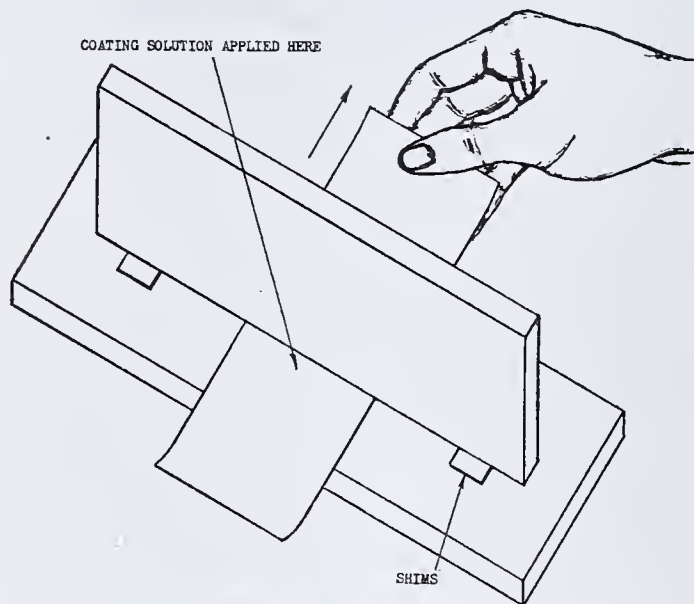


FIGURE 1. APPARATUS

from a base of moisture-proofed regenerated cellulose, whereas the films from nonaqueous solutions might well be stripped from a sheet of plain cellulose, as Sager has described. In the author's laboratory the method has been used principally for the preparation of samples of coated papers and other sheet materials. The method dispenses with equipment for stretching the regenerated cellulose base, permits contraction of the film during drying and thus eliminates drying strains, and facilitates the production of films of essentially reproducible thickness.

It is convenient to spread films from aqueous dispersions upon a moisture-proofed regenerated cellulose sheet, using a device (Figure 1) which consists of a steel bed plate  $12 \times 4 \times 1.25$  inches and a spreading bar  $10 \times 3 \times 0.5$  inches. This device is used by resting the spreader bar on its edge, with its face perpendicular to the bed plate and separated from it by the use of thin shims, the thickness of which will regulate the amount of coating applied. The cellulose sheet is placed under the spreading bar between the shims, and an excess of the film-forming solution is poured on it and spread with a spatula across the width of the sheet. The sheet is drawn between the plates with a uniform motion and the coating is permitted to dry.

The thickness of liquid film applied has been found to approach the difference in thickness between the shims and the base sheet, but never to equal it. The contraction is probably due to the formation of a stationary film in contact with the spreading bar. With bases that tend to pucker or curl, it has been found advantageous to use solutions of appreciable viscosity and to pull the sheet through with a rapid motion. The base material should be pulled through straight and parallel with the base plate in order to avoid wrinkling the sheet or interfering with the thickness of liquid film applied, as determined by the spacing of the spreader bar.

## Apparatus for Testing Crushing Strength of Granules

E. F. HARFORD

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THE increasing interest in granulation of various materials has created a need for methods of production control and evaluation of granule characteristics. One of the chief properties with which both producer and consumer are concerned is the hardness of the individual granules—i. e., the resistance to destruction during normal shipping and handling. An instrument for quantitative expression of granule crushing strength therefore should serve a useful purpose. Previous methods employed in this laboratory for the determination of ultimate compression lacked the desired speed and accuracy.

The simplest determination of granule crushing strength is accomplished by placing the grain between plates and piling weights on the top plate until failure occurs. Materials of construction such as concrete, cast iron, etc., are tested for ultimate compression in such equipment as the Adie (3) or Wicksteed (1) single-lever testing machine. However, no instruments of this type have been constructed to operate within the range desired for the granules or briquets made from finely divided materials.

The present apparatus was designed as a simple compression tester without sacrificing the necessary speed, convenience, and reproducibility.

## Description of Apparatus

As shown in Figure 1, the apparatus consists of a first-class lever, pivoted in the center. The applied force acting upwards on one end is a direct function of the granule resistance to crush-



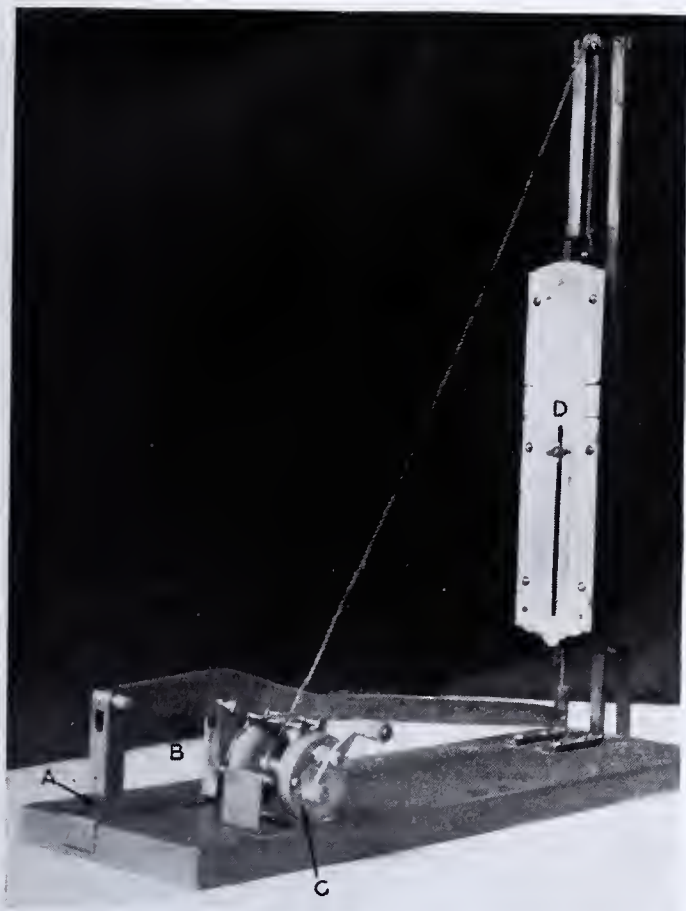


FIGURE 1

ing on the other. A granule is placed on the plate, A, directly beneath one end of the lever, B, and the load is applied on the opposite end at a uniform rate by winding the string on a small reel, C, until failure occurs. A spring balance, D, connected in the reel system and sliding in upright supports, registers the amount of load applied at that end of the lever. It was found convenient to use lever arm ratios of 4 and 8 to 1 and consequently the balance reading was multiplied by 4 or 8 as the case may be. The capacity of the instrument illustrated was 2000 grams with a lever ratio of 4 to 1 and 4000 grams with a lever ratio of 8 to 1.

### Reproducibility of Determinations

Numerous samples of widely differing materials were selected for testing the reproducibility of the crushing strength determinations. The reproducibility of determinations depended on the number of granules included in the average. It was found that maximum deviations from the averages of fifteen granules of each material tested were approximately  $\pm 8$  per cent. Still closer agreement was obtained by crushing 20 granules, which resulted in reduction of the maximum deviation to around  $\pm 6$  per cent. For example, a material with a crushing strength around 850 grams gave averages ranging from 800 to 930 grams with 15 granules and from 830 to 930 with 20 granules. This small increase probably cannot justify the extra time required to crush larger numbers of granules. Although crushing strengths of individual granules varied from 480 to 1560 grams, in the above example the averages of 15 to 20 granules were satisfactorily reproducible.

The accuracy of the method also depends on close grading of the granules by screening. A relationship between granules of different screen sizes probably may be determined from the formula  $P = Cd^N$  (2), where  $P$  is the load on a single grain and  $C$  is a coefficient having a value which may be determined experimentally. The value of  $N$  for ball bearings is 2 but for granular materials it may vary from 1 to 2 depending on the material and method of granulation.

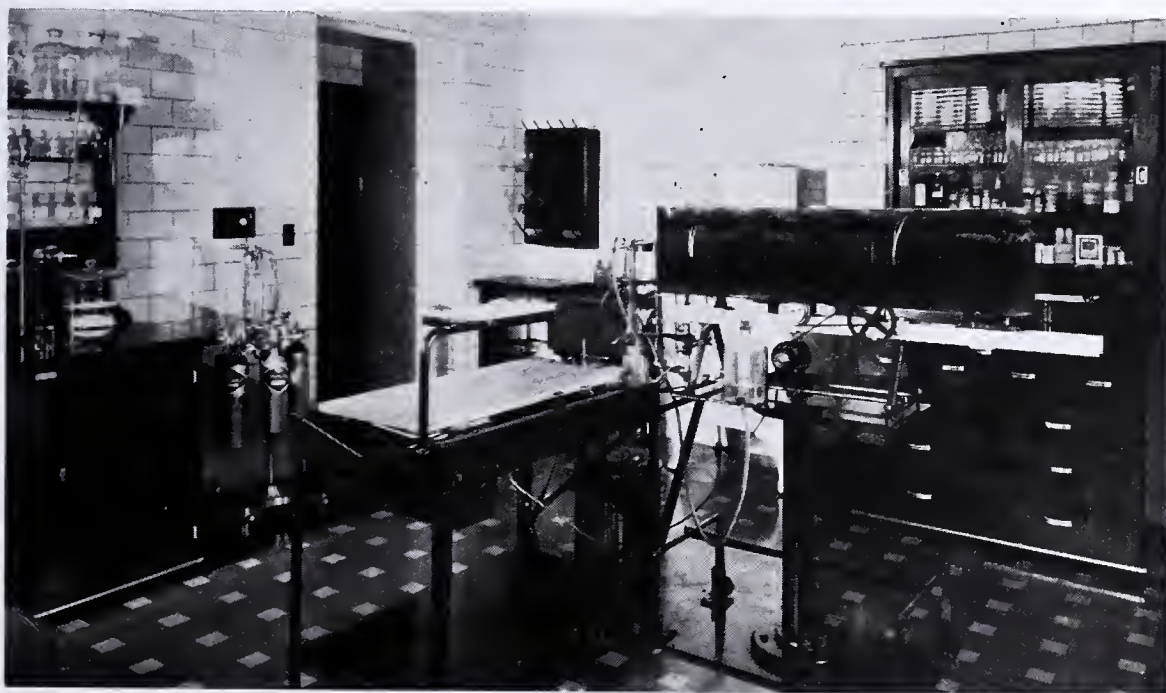
### Application of the Tester

This apparatus should be useful in investigating the influence of absorbed moisture, compounding, mechanical methods of production, and other factors on the crushing strength and handling or storage characteristics of granular or briquetted pharmaceuticals, foods, fertilizers, and fuels.

### Literature Cited

- (1) Batson and Hyde, "Mechanical Testing," Vol. I, p. 48, New York, E. P. Dutton & Co., 1922.
- (2) Marks, "Mechanical Engineers' Handbook," pp. 715-16, New York, McGraw-Hill Book Co., 1916.
- (3) Morley, "Strength of Materials," pp. 519-20, London, Longmans, Green & Co., 1921.

RECEIVED October 6, 1937.



*Courtesy, Lilly Research Laboratories, Indianapolis, Ind.*

### GENERAL VIEW OF ONE OF THE PHARMACOLOGIC RESEARCH LABORATORIES

Operating table and large variable-speed kymograph apparatus for recording the effects of drugs over several hours. Changes in blood pressure, respiration, etc., can be permanently recorded in this manner.



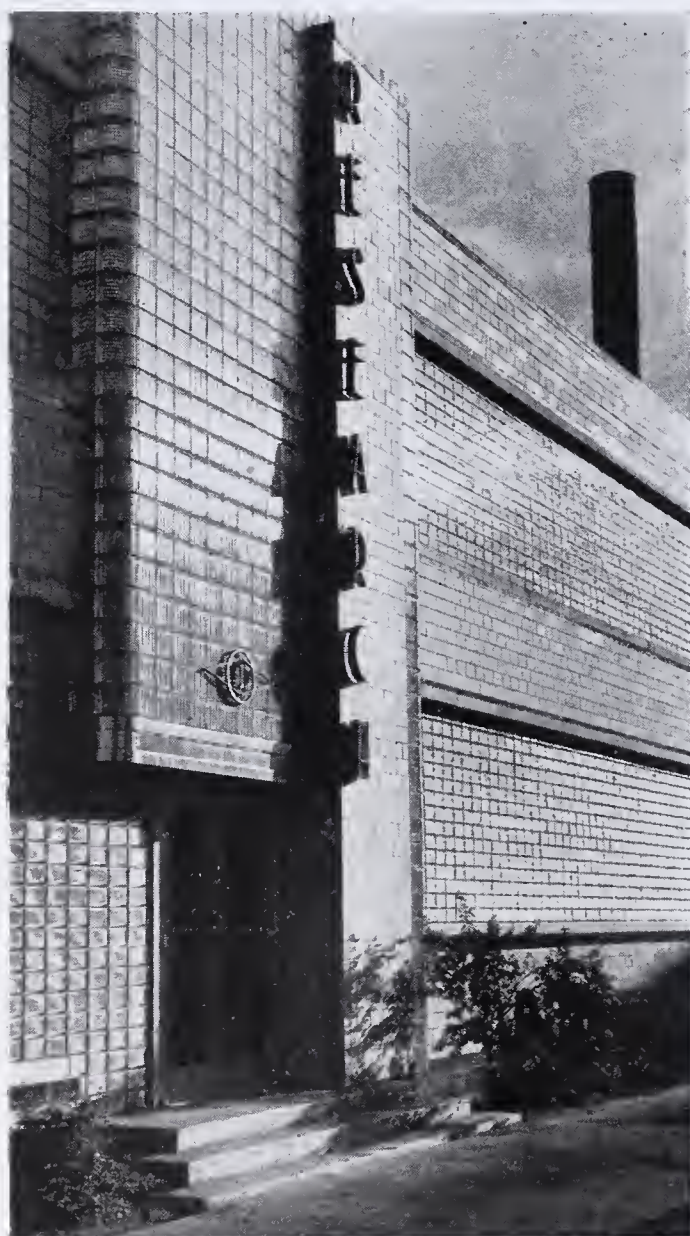
# Modern

# Laboratories

## Industrial and Structural Products Laboratory of the Owens-Illinois Glass Company

H. C. WINSOR

Owens-Illinois Glass Co., Newark, Ohio



MAIN ENTRANCE

THE Industrial and Structural Products Laboratory of the Owens-Illinois Glass Co., at Newark, Ohio, is in reality the research, development, and central unit of the plant, devoted to the manufacture of fiber glass and its uses. It is unique in its application of glass in the construction of the building, which presents to the view a solid, compact structure, constructed mainly of glass block, interspersed by sections of cream-toned brick. Running the full height of the building on one side of the main entrance are cast-aluminum letters spelling "RESEARCH."

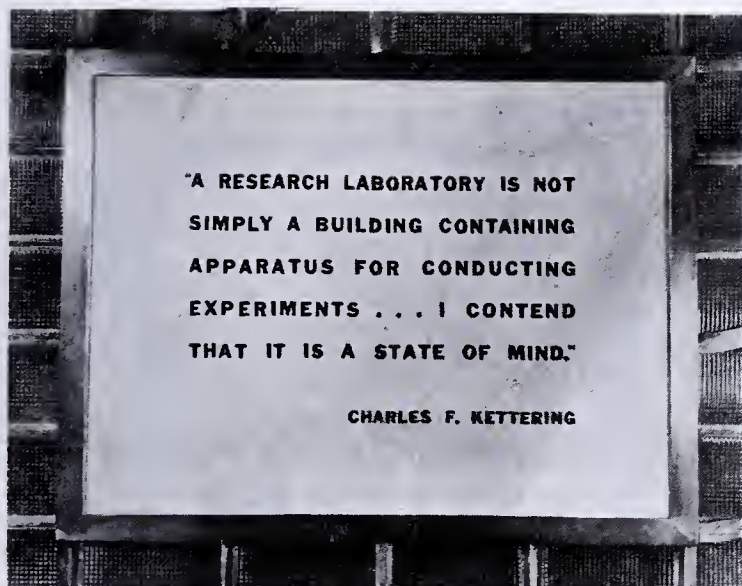
Just inside the main entryway of the office building is a glass-cloth plaque, upon which is printed: "A research laboratory is not simply a building containing apparatus for conducting experiments . . . I contend that it is a state of mind.—Charles F. Kettering." Everything possible has been done to make the building conducive to this state of mind.

The front portion of the building is devoted to offices and a small chemical laboratory, while the rear houses a relatively large machine shop, in which the main machinery for the plant as a whole is made. Departments are definitely correlated for carrying on the business of research, with special emphasis on producing ideal conditions for the processes of thinking and trying.

The floors are surfaced with rubber tile for the foot comfort of employees. The ceilings of both floors are finished with glass acoustical tile of a high sound-absorption coefficient, so that noise within this structure is at a minimum. In the ceilings are also 4-inch thicknesses of glass insulating wool, which keeps heat or cold from passing promiscuously from one floor to the other or to the outside. The glass-block walls admit a light which is diffused and comparable to the lights of a northerly exposed window or skylight. The reduction of glare and shadow with Insulux block promotes comfort, efficiency, and quality workmanship and is particularly desirable for close work. In general, the light transmitted by Insulux is controlled by the face pattern of the block. The amount of incident light transmitted by the various patterns ranges from 86.5 to 27.6 per cent. The prismatic pattern of the block used in this building admits 78.5 per cent of all incident light, diffusing it to all corners of each room.

Air infiltration is reduced to a minimum. With these glass-





ing unit does a very complete job in keeping a fresh, uniform temperature throughout the building. The purity of the air is ensured by the use of Owens-Illinois Dustop air filters, which catch 95 per cent of the dust in the air which passes through them.

Most partitions between the offices consist of plate glass, so that the view is practically unobstructed from one office to any other in the building. Since the business of research requires constant gatherings and conferences, it is a great help to the employees as well as the management to be in almost constant visual contact. However, the acoustical treatment makes the natural tones of the human voice inaudible. All window frames, doors, and door frames are of hollow metal, painted to match the gloss brown of the trim brick. The plate glass is mounted in rattle-proof and moisture-proof rubber channels. Although the building is of fireproof construction, as a further safeguard an automatic sprinkler system is installed with outlets in the ceilings of the offices and halls.



CHEMICAL LABORATORY

The chemical laboratory, located on the first floor of the main office building, is very well equipped to carry on analysis relative to the company's business as well as experimental melting of new types of batches. If the batch is proved satisfactory in this very small way, it is then tried in larger amounts in the experimental furnaces, which are located at the other end of the structure. If the material proves itself here, it is then out of the experimental or laboratory state and is ready to be used in the factory on a commercial basis.

The testing laboratory, located next to the store-room on the first floor, is

block walls, there is nothing to paint, no attachments or mechanical parts to keep in condition, nothing to rust out or replace; light-giving panels are easily cleaned, and a permanent, dependable part of the structure. The vacuum within the block presents excellent heat-retarding qualities.

The lighting plan was designed on a 20-candlepower minimum throughout. All lighting in the office building and engineering department is indirect from fixtures suspended from the ceiling. The glass-fiber acoustical ceiling material provides an excellent light-diffusing background.

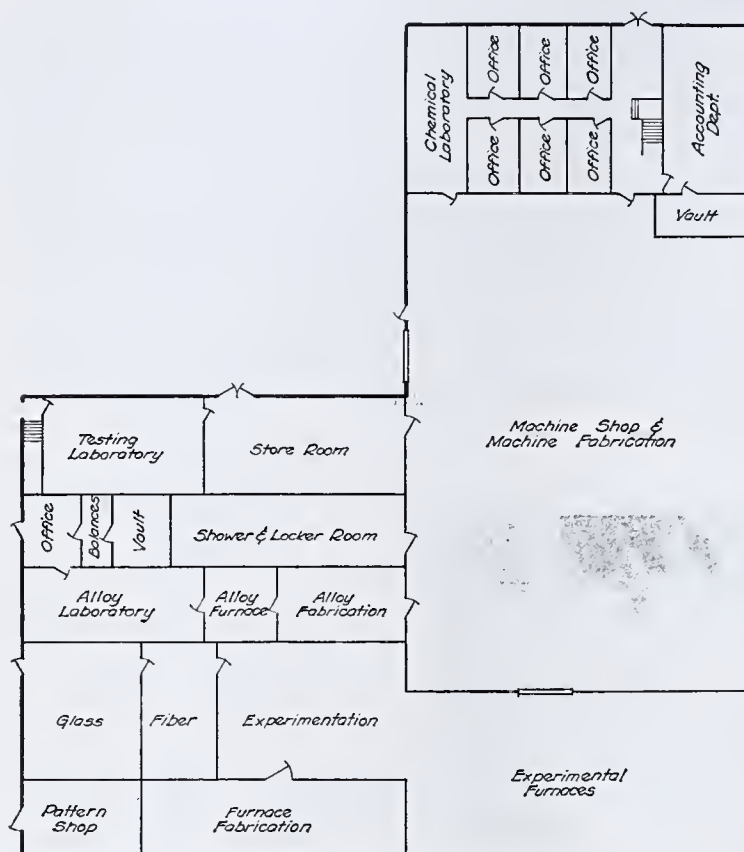
In the machine shop, the glass-block wall permits complete utilization of floor space. By promoting a more uniform inside temperature, it permits placing the machines closer to outside walls, and also helps avoid temperature changes arising from outside changes. Insulux is translucent, not transparent, and therefore admits light without the disadvantage of outside view. With all this insulation assistance, the air-condition-



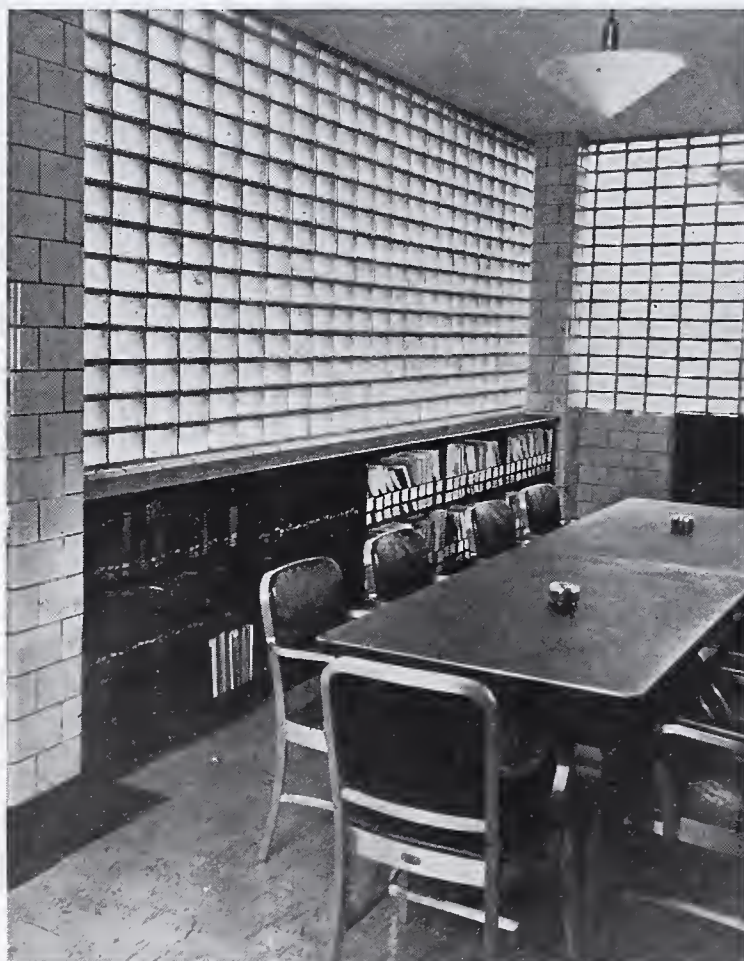
OFFICE



devoted mainly to thermal conductivity tests. It is large enough so that materials may be tested for heat coefficient in their actual state of commercial application. Examples



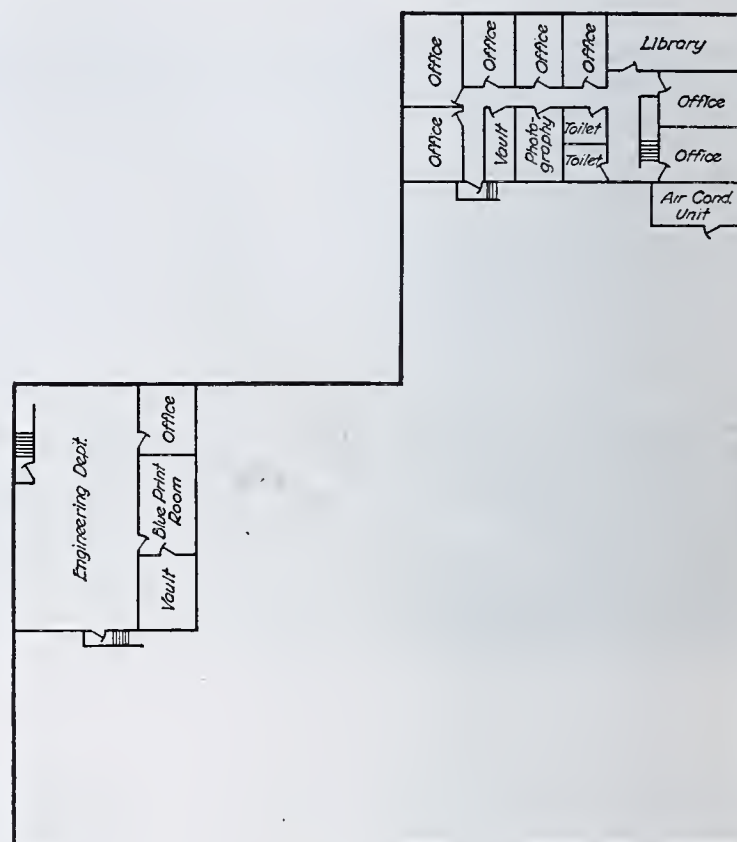
FIRST FLOOR PLAN



LIBRARY

of this are stoves and refrigerators which are constantly brought in and insulated with Fiberglas and competitive products and then compared for efficiency. Means are provided for maintaining steady room temperature and humidity conditions, which are very helpful in obtaining reliable results.

In the engineering department, practically all of the company's machinery is planned by its own engineers and then is built by machinists in the adjacent machine shop. This department, which is next to the machine shop, is very similar to the office building on the inside except that it is not quite as large nor broken up into so many offices. The upstairs consists of a large drafting room, skirted by a glass-enclosed office, blueprint room, and vault. The lower part is broken up into a modern shower and locker room for the employees, a storeroom, a testing laboratory, and two precious-metal departments which have a late type of bank vault for storing valuable laboratory materials and information.

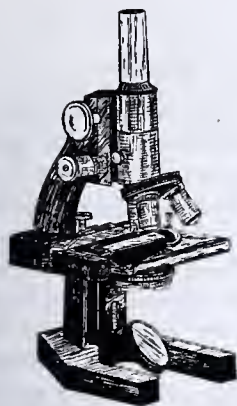


SECOND FLOOR PLAN

The roof of this building is similar to that of the office building. It is a built-up, 20-year-bonded roof, concealed by a parapet wall around the building.

The extreme south portion of the laboratory building is devoted to actual production experiments. Here are found different types and shapes of furnaces for the production of Fiberglas. New ideas with respect to furnaces are tried and proved here before final adoption in the factory. The roof of the machine shop differs from that of the rest of the structure in that it is rounded, made of a composition in corrugated form, and is supported by an arch truss of structural steel. Below the arch ribs and purlins of the roof construction is a suspended ceiling of glass wool held in place by an expanded metal mesh. The heat transmission through this type of construction is relatively negligible and because of its economy of construction provides an ideal machine-shop ceiling.





# Microchemistry

## Determination of the Size of Fine Abrasive Powders

### A Comparative Study of Microprojection and Sedimentation Methods

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THE determination of the size of particles finer than 325-mesh is usually carried out with a microscope or by calculating the size from the rate at which the particles settle in a liquid or air. This report considers some of the differences in the size-distribution curves that were prepared for aluminum oxide abrasive powders using a conventional microprojection method and a common sedimentation method. The abrasive grain manufacturers and the users of fine abrasive powders have a standard method of checking and controlling the size grades, according to which the size-distribution curve is computed from sedimentation tube data. According to this procedure, methanol of special purity is the liquid through which the carefully dispersed abrasive settles, and the rate of accumulation of the grain at the base of the tube is observed. The glass sedimentation tube is 2 cm. in internal diameter and 94 cm. long. A collecting tube 11 mm. in internal diameter and tapering to a graduated neck 4 mm. in diameter is mounted at the bottom of the sedimentation tube. The sedimentation tube is water-jacketed for temperature control.

In setting up standard specifications for the natural corundum abrasives produced for use in the optical industry, however, it was considered advisable to employ a microscopic method of determining grain size. The microscope is the standard instrument in this industrial field and the specialists responsible for the separation of the various size grades of corundum are accustomed to rely upon it as a control instrument. Then, too, as the finest grades of corundum used in precision grinding of glass or metal surfaces are composed of grains with an average diameter less than 10 microns, the dispersion of such material in a liquid is difficult and incomplete. The time required for the settling of the portion of the sample less than 5 microns in diameter is excessive.

#### Microprojection Apparatus for Fine Abrasives

A standard plant control procedure has been developed that is an adaptation of the method employed by Work (1) in studying fine powders. An ordinary microscope is used with a Bausch & Lomb model B microprojector support. A reflecting prism fits over the microscope eyepiece to direct the beam of light to the screen. A clock-feed arc lamp operated from an 8-ampere rheostat is the means of providing illumination. The model B microprojector carries a condensing lens by means of which the light from the arc is sharply focused through a fixed mirror onto the iris diaphragm of the microscope substage. A water cell absorbs heat from the light beam. When the microscope is fitted with a 16-mm. apochromatic objective and a  $\times 7.5$  compensating eye-

piece, a comparatively flat field is obtained. The distance to the screen for the desired magnification is adjusted by focusing the microscope on a stage micrometer, a glass slide ruled with lines 10 microns apart. The projection screen is ruled at intervals of 10 mm. and, when the projected lines fall on the rulings of the screen, a total magnification of  $\times 1000$  is assured.

#### Preparation of Slides

A method of slide preparation developed by the abrasive industry is suitable for use with this method.

The dry powder is sampled carefully, the sample is reduced in size by quartering, and a small metal cup is used to pick up enough material to form a layer on the slide with few particles touching or overlapping. A clean glass slide is placed on a horizontal surface and covered with a brass tube 8.75 cm. (3.5 inches) in diameter and 50 cm. (20 inches) long. The top of the tube is closed with a rubber stopper through which projects the lower end of a glass tube, whose upper portion is bent to the shape of a sink trap. The sample of abrasive is placed in the bend of the trap and a sharp puff of air from a rubber bulb forces the fine powder into the upper portion of the brass tube. The grains settle through the air in the tube, forming an evenly distributed layer on the glass microscope slide. The amount of sample is chosen so that particles do not touch or overlap to any great extent. Two slides are prepared and protected under a watch glass until they are placed on the mechanical stage of the microscope. From 10 to 20 fields are selected at random on each slide and the diameter of the grains is measured. The distribution of the different sizes of grain on the slide has been found to be very uniform. Drying the original sample in a crucible heated over a flame will overcome the tendency of very fine powders to collect in clumps and aggregates.

#### Determination of Average Diameter

The particle diameter is measured on the projection screen with a millimeter rule. If the grain is not symmetrical, the average of the longest and shortest dimensions is taken as the diameter. It is convenient to have the microscope fitted with an extension focusing rod, so that exceptionally large or small grains can be brought into sharp focus. Fine abrasive powders are made to be rather uniform in size and if the iris diaphragm of the substage condenser is partially closed the depth of focus of the system is such that many grains will be in focus simultaneously.

The collection of data is facilitated if an observer measures and calls out grain diameters at the screen as a helper puts a mark under the corresponding data sheet column. When



more than 100 grains of any single micron size have been measured, the count is stopped. The total grains measured for a determination vary from 200 to 2000, depending on whether the sample contains a few sizes or many sizes. Well-graded abrasives do not require the measurement of a large number of grains. The number of each micron size counted is multiplied by the cube of the diameter to obtain the relative amount of that size by volume or weight present in the sample and the percentage of the total amount is calculated for each micron size. To obtain the size data in the form of an accumulation curve, such as the abrasive industry uses, the percentage of the total sample larger than each size is plotted against the diameter in microns.

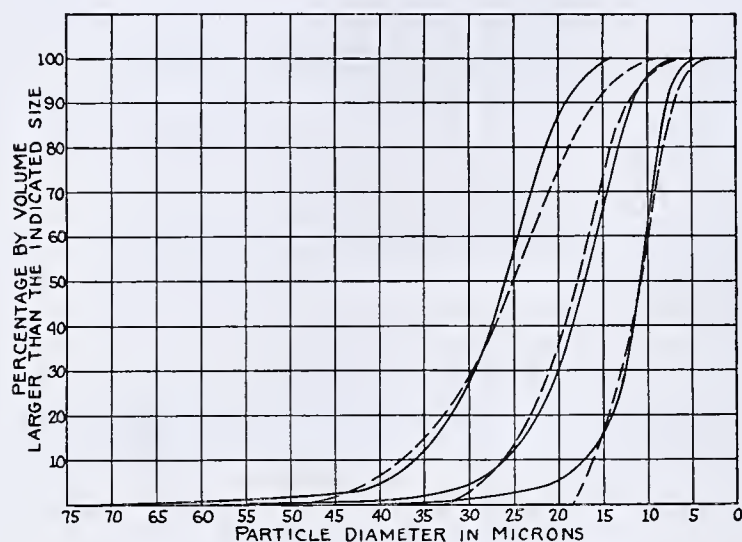


FIGURE 1. SIZE-DISTRIBUTION CURVES FOR FINE ALUMINUM OXIDE

1. Solid curve calculated from sedimentation tube data
2. Broken curve calculated from microprojector data

There are many ways of calculating and expressing average diameter and the term thus has no uniform meaning. The buyers of abrasive powder use the term "average diameter" to designate the particle diameter corresponding to the point at which the accumulation curve crosses the 50 per cent line.

### Comparison of Methods

To ascertain if the size as measured by microscopic projection is similar to that determined by the standard sedimentation method, various abrasive companies were asked to run a sample of graded aluminum oxide by the sedimentation method and send it to the author as an unknown for microscopic measurement. For samples consisting of grains approximately symmetrical in shape, such as would be obtained by grinding wet corundum in a ball mill, there was good agreement in the figures for average diameter as determined by the two methods. This agreement was within the limit of error of the methods. The shape of the size-distribution curve was characteristically different, however, depending on the method of measurement. The percentage of fine particles was greater when measured microscopically. The difficulties in dispersing fine particles individually in a liquid and the tendency of large grains to carry fine material with them in settling would explain the failure of the sedimentation method to reveal all the fine particles present in the sample. Notwithstanding the great care used in selecting the settling medium and the care taken to clean the grain by ignition, which make this particular sedimentation method especially free from coagulation troubles, the percentage of fine material indicated by it is low. In the coarse portion of the distribution curve the sedimentation data show more large particles than do the microscopic data.

### Effect of Irregular Grain Shape

For grinding optical glass surfaces a symmetrical abrasive grain is used. For some types of abrasive paper, however, the grains are purposely made irregular in shape, including both thin flakes and elongated particles. All agreement between the standard sedimentation test and the photomicrographic method of determining grain size described above disappears when the sample is composed of such long, narrow, irregularly shaped grains. The size number obtained from the accumulation curve is much larger when the curve is drawn from microprojector data than when the curve is computed from the sedimentation tube data. Even when the smallest visible dimension of the particle under the microscope is substituted for the average of the longest and shortest dimensions as the size of the particle, the size-distribution curves obtained by the two methods do not agree. Figures 1 and 2 indicate the agreement in size curves with symmetrically shaped abrasive powders and the difference in size curves with irregularly shaped particles when the same sample is measured by sedimentation tube and by the microscope. There is little point in saying that one method is more accurate than the other for irregular grains.

### Advantages of the Microprojection Method

All the abrasives used in an optical plant are of the more symmetrical grain shape. The fact that many of the samples to be examined are below 10 microns in average particle size has led to the adoption of a microprojection method for determining the size-distribution curves used in controlling plant production of corundum for optical grinding. In this size range the grading is close, only a few particle sizes are found in a sample, and the number of particles to be measured to obtain a smooth size-distribution curve is low. Results are reproducible within 1 micron for plant samples. The time that is needed to prepare the sample, measure the grains, and compute the accumulation curve is less than 2 hours. There is no uncertainty about the quality of a reagent (such as the methanol used in the sedimentation method) nor about the dispersion of the grains in the liquid. For coarse abrasives the number to be counted is larger and the time required may be longer unless a lower magnification than  $\times 1000$  is used. The shape and structure of the abrasive grain can be observed during the size determination and lots containing poorly

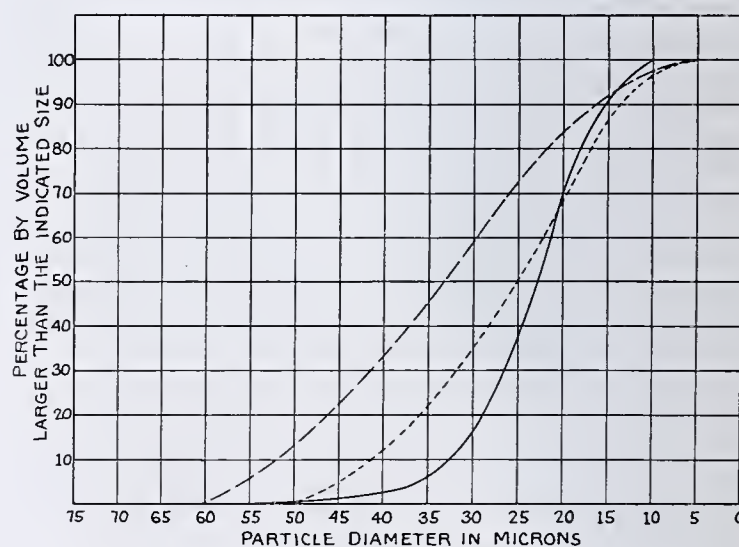


FIGURE 2. SIZE-DISTRIBUTION CURVES FOR ABRASIVE GRAIN CONTAINING MANY LONG OR NARROW SHAPES

1. Solid curve from sedimentation tube data
2. Broken curve from microprojector data. Average of long and short dimensions taken as average diameter of particle
3. Dotted curve from microprojector data. Smallest visible dimension taken as average diameter of particle



shaped particles rejected. A microscopical determination of the size-distribution curve of a fine abrasive powder requires no more skill and care in manipulation than does a determination of equal accuracy by the sedimentation method. Size numbers obtained by the two methods are in close agreement for symmetrically shaped abrasives.

For abrasive flours coarser than those shown in Figures 1

and 2 the sedimentation tube method is relatively rapid and easy to carry out.

### Literature Cited

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# Microchemical Analysis of Colored Specks and Crystalline Occlusions in Soap Bars

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THE emphasis in the microchemical literature is usually placed on the description of new methods or on the development of special apparatus. The practical application of these methods to the solution of analytical problems which cannot be solved by the usual methods is seldom mentioned, except in the analysis of valuable objects of art, etc. The present paper describes two cases which illustrate the practical value of the so-called "classical" micromethods. Considerable time and effort spent in the application of ordinary methods of analysis to these two problems failed to yield a solution. Since the difficulties entailed the loss of a large amount of merchandise, a discovery of the cause was of considerable importance to the manufacturer. Micromethods of analysis were therefore used and in a comparatively short time yielded the necessary data for locating the source and preventing a further recurrence of the trouble. The final solution may seem surprisingly simple.

In the following discussion, only deviations from known microprocedures are described in detail.

## Qualitative Microchemical Analysis of Colored Specks in Soap Bars

**SAMPLE.** Colored specks were distributed on and in a single soap bar, from which they were isolated by cutting the soap in such a way that at least one surface of the particle was exposed. Under the binocular microscope the specks were lifted off with fine needles and collected on a microculture slide with a small concavity. About 35 such specks, a few of them pure soap only, were submitted for microanalysis. Investigation under the microscope showed several types of particles which are illustrated in Figure 1. With the microchemical manipulator designed by one of the authors (1) all *b*, *d*, and *e* particles were separated, and then the major part of the adherent white material was removed under the binocular microscope (magnification,  $\times 30$ ). In order to obtain preliminary information on the ingredients and technic best suited to the problem, the white particles were analyzed first.

**ANALYSIS OF WHITE PARTICLES.** About 15 white particles, *a*, and separated white portions *d* and *e* collected in a platinum dish 10 mm. in diameter, weighed 48 micrograms. With 20 micrograms of this sample a qualitative organic elementary analysis was carried out, using Emich's procedures (5, 6) and some modifications by Alber for estimating the percentages of

the elements, which will be described in a future publication. The analysis showed the following results: carbon, ++; hydrogen, +; halogen, -; nitrogen, -; phosphorus, -; sulfur, ++ (the strength in each test is indicated by +++, over 25 per cent; ++, 10 to 25 per cent; +, 1 to 10 per cent; -, negative reaction).

Emich's sulfur test consists in oxidizing the sulfur of the organic compound to sulfate by heating with nitric acid in a sealed capillary; since the temperature should not exceed 300° C., the test can be carried out just as accurately in less expensive Pyrex glass capillaries of about 1-mm. wall thickness and 1- to 2-mm. bore, with the usual precautions. By comparing the length of the barium sulfate column with those produced from known amounts of sulfur-containing materials, an estimation of the sulfur content within the given limits is easily made. The supernatant liquid is transferred to another capillary and the phosphate is precipitated and estimated as ammonium phosphomolybdate by comparison with known amounts of phosphorus-containing substances.

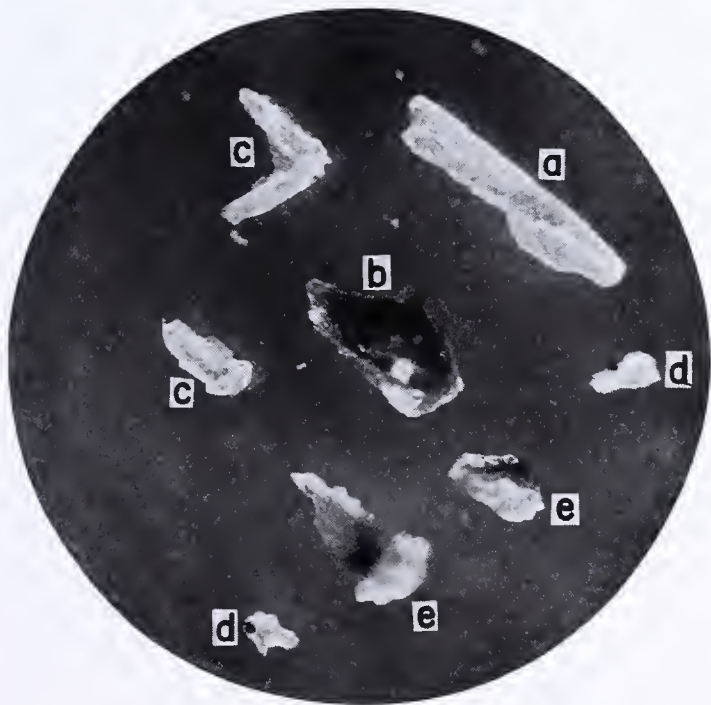


FIGURE 1. COLORED SPECKS ISOLATED FROM SOAP ( $\times 20$ )

Taken with a Reichert photomicrographic apparatus in reflected light

- Pure white particles without any special structure
- Reddish brown and dark-brown particles, uniformly colored throughout
- Very slightly yellow particles
- White particles with very small dark spots, which appear black, sometimes dark green in reflected light. The dark specks have distinct boundaries, but are apparently isotropic in polarized light
- Different combinations of the above types, such as white or yellow particles with brownish portions, the color of which shades off gradually

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The remaining 28 micrograms of white particles were carefully ashed on a metal block, leaving a white residue weighing approximately 4 micrograms (observation in reflected light under the microscope). The solution of this residue in *N* hydrochloric acid was used for the following tests: sodium test with magnesium uranyl acetate, ++; sulfate test with barium nitrate, ++; flame test (hand spectroscopy), sodium present alone. Tests for groups 1, 2, and 3 with Emich's fiber technic (1, 3, 5, 6) gave negative results. This "group indicator method" has been successfully used throughout the investigation. Since the precipitates on the fiber ends can be redissolved, even the smallest amounts are not sacrificed.

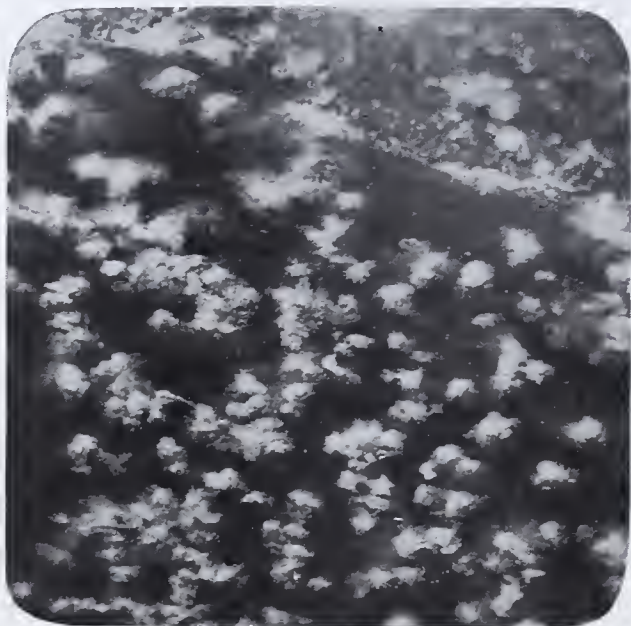


FIGURE 2. DENDRITIC CRYSTALLINE OCCLUSIONS IN SOAP BARS ( $\times 7$ )

Photomicrograph in reflected light with a green filter

It was concluded that the white particles were pure soap with sodium sulfate as an inorganic constituent.

**ANALYSIS OF BROWN AND BLACK PARTICLES.** About 20 colored specks (*b*, *c*, and separated dark spots *d* and *e*, but not including the one brown particle, *b*, shown in Figure 1) weighed 59 micrograms. When the sample was carefully treated with nitric acid and sulfuric acid in a platinum dish on the water bath, a slight reaction on the black particles was noticed. Complete ashing at about 600° C. gave a residue of 32 micrograms, which formed colored zones, a dark-red inner, bright-red center, and white outer ring (oxides, sulfates). The water-soluble part was extracted with 0.5 ml. of distilled water; the extract gave a positive sodium test and a positive sulfate test, so that most of the white residue consisted of sodium sulfate. The remaining material was only partially soluble in nitric acid (1 to 1). Treatment with hydrochloric acid (1 to 1) dissolved all except a few colored spots, which were brought into solution by fusing with sodium borate and dissolving this borax bead in diluted hydrochloric acid (1 to 10). The platinum dish lost about 20 micrograms during these manipulations; the platinum was detected in the analytical procedure to the extent of more than 10 micrograms (Table I). All the solutions were combined in a 1-ml. centrifuge cone, evaporated to dryness, and dissolved again in 0.2 *M* hydrochloric acid; since no residue remained, the absence of group 1 was established.

About 1 cu. mm.—i. e., one-tenth of the acid solution—was evaporated on the end of a cotton fiber. The substance, collected on the fiber tip, was exposed to ammonium sulfide by drawing the fiber through the reagent droplet three or four times, forming a black precipitate (all observations on the fibers were made under the microscope in transmitted and reflected light with various colored backgrounds, 1). One cubic millimeter of hydrochloric acid partially dissolved the sulfides, indicating the presence of groups 2 and 3. The remaining precipitate on the fiber end was treated with a droplet of aqua regia, and both solutions were combined with the original sample.

The resulting acid solution was analyzed according to a modification of the qualitative microscheme of Benedetti-Pichler and Spikes (3), which allows a quantitative estimation

of the constituents within 5 per cent (relative). The microtechnic of working in centrifuge cones, as described above, introduces the possibility of a less accurate estimation through losses by adsorption on the comparatively large wall surfaces, since the total weight of the elements present is so small. In the final steps of the identification and comparison with known amounts, smaller vessels with less surface were utilized, and corresponding reductions in the amounts of the reagents were made. Fine capillaries of 0.5-mm. bore allowed a differentiation in the lower region of concentrations between 5, 3, 1, 0.5, and 0.1 micrograms, and permitted their comparison with known quantities of the same element. Confirmatory tests on the isolated precipitates were carried out by means of color reactions with Feigl's drop-test technic (1, 7). If the absence of certain elements was obvious, the procedure for these groups was shortened—e. g., in the arsenic group no yellow or orange sulfide precipitate could be noticed, thus eliminating the specific tests for arsenic and antimony. The only unexpected difficulty in the course of the analysis was the appearance of platinum, which, at the time of the experimental work, was not included in the original scheme. Benedetti-Pichler (2) has described a finer microtechnic for 1-microgram solid samples and 0.01-cu. mm. reagent portions, which must be measured and handled with the use of Chamber's micromanipulator.

A special analysis of one single brown speck (*b*, Figure 1) showed the presence of more soap (carbon, ++; sodium, ++; sulfate, +; chromium, —; iron, ++) than in the black particles, as well as the absence of chromium. This one particle was ashed on a quartz slide to prevent the disturbing influence of platinum. The same precaution was used in the ashing of a test sample of similar composition, as revealed by the analysis of the main portion of the colored specks. Such analysis of a known mixture seemed necessary in order to prove that it was permissible to make comparison tests for the estimation of such small quantities. To some extent, it also showed the precision of the modified microtechnic, although many more such test analyses would have been necessary.

Table I indicates the results of analyzing the main portion of the colored specks, the confirmatory tests for the different elements, and the results of the test analysis.

TABLE I. ANALYTICAL RESULTS

Elements Tested for	Found in Main Sample $\mu\text{g.}$	Confirmatory Tests (7)	Results of Test Analysis Present $\mu\text{g.}$	Found $\mu\text{g.}$
Na	+	Spectroscope	3	1
Group 1	—	—	—	—
Sn	1–0.5	Flame test	2	More than 1
Pt <sup>a</sup>	More than 10	—	—	—
Pb	0.5	Dithizone	1	1–0.5
Cu	—	—	—	—
Bi <sup>b</sup>	(0.1)	Fiber test (2)	—	0.5–0.1
Co	1–0.5	Rubeanic acid	1	1
Ni	—	—	—	—
Fe	15	$\alpha, \alpha'$ -dipyridyl	20	More than 15
Mn	—	—	1	3
Cr	1–3	Diphenylcarbazide	1	1
Zn	<sup>c</sup>	—	—	—
Al	<sup>c</sup>	Morin (5)	2	1
Group 4	—	Spectroscope	Ca = 3	5
C—H	+	—	Stearic acid = 10	++
Total	About 20	—	34	About 31

N, P, halogen = negative.

<sup>a</sup> Not present in original sample; introduced from platinum vessel (loss = 20  $\mu\text{g.}$ ).

<sup>b</sup> Probably introduced by an impure reagent, as seen from the test analysis.

<sup>c</sup> Not tested for, since solution was lost by an accident; no indication of the presence of these two elements in any step of the analysis.

It was concluded that the brown specks, *b* and probably also *c*, consisted mainly of soap colored with iron. The black specks contained very little soap; the main constituent was iron with 5 to 10 per cent of chromium, 5 per cent of cobalt, 1 to 5 per cent of lead and tin, and small amounts of sodium sulfate from adherent soap. The source of these contaminations in the soap bars could be traced by the analytical results,



and further disturbances during the process of manufacturing eliminated.

### Microchemical Analysis of Crystalline Occlusions in Soap Bars

**QUALITATIVE.** The crystalline occlusions were dendritic in form, as shown in Figure 2, and appeared in a surface layer approximately 1 mm. thick on the soap bars; these crystals appear to be the result of efflorescence. The sampling of these very tiny crystals was difficult because of their enclosure in the soap. Since no special mechanical device was applied for the sampling, it took about 6 hours to collect the material necessary for a preliminary qualitative analysis. Crystal aggregates from several bars of soap were lifted out with a spear-shaped dissecting needle. In the same way samples of soap without crystals were taken from the surrounding areas.

**Analytical Procedure.** Both samples were ashed with sulfuric acid in platinum macrocrucibles. As the residue determinations indicated that some inorganic material constituted the major portion of the crystals, it was decided to run a qualitative analysis on the ash, in both cases using the unmodified analytical scheme of Benedetti-Pichler and Spikes (3). The results of these analyses are shown in Table II. The composition of pure soap from bars containing crystals and from bars without any crystals was found to be identical, as established by a special set of analyses. The method of sampling, however, did not warrant drawing accurate conclusions from the qualitative analysis. The authors wish to thank W. F. Spikes for performing the major portion of the qualitative analysis (1935).

TABLE II. QUALITATIVE ANALYSIS

	Crystals Contaminated with Soap	Soap without Crystals
Weight of sample, mg.	21.103	21.091
Weight of residue, mg.	5.695	5.278
Residue, %	27.0	25.0
Main constituent	Sodium	Sodium
Other constituent	50 $\mu$ g. tin	10 $\mu$ g. tin
Traces	Aluminum, molybdenum, chromium	Aluminum, molybdenum, chromium

**QUANTITATIVE.** At this point it was decided to obtain some of the crystals in as pure a state as possible and to perform a quantitative microchemical analysis of the constituents. The type of analytical work required could not be anticipated, but had to be chosen while going through the different steps of the procedure. The crystals for these determinations were all taken from the surface of soap bars, where, during efflorescence, the soap film covering the crystals had ruptured. A binocular microscope (magnification,  $\times 30$ ) served to control the isolation and removal of the crystalline occlusions with a dissecting needle. About 140 bars of soap were used in order to collect 1.376 mg. of these crystals, as free as possible from soap; this procedure required about 60 hours.

The results of the qualitative analysis (Table II) led primarily to the conclusion that tin soap was present in the crystals. Because of the insolubility of tin soap in cold water, a moisture determination (volatile matter at 105° C.), an analysis of the water-soluble products, and a carbon and hydrogen determination, as well as a tin determination in the water-insoluble material, seemed necessary to confirm this opinion.

As, with such a small sample, too frequent changes of the reaction vessels were undesirable, a special platinum boat was prepared by piercing the bottom of an ordinary platinum microboat for carbon and hydrogen determinations (8) 27 times with a fine needle. A platinum-sponge filtering layer about 0.75 mm. thick was superimposed on this perforated

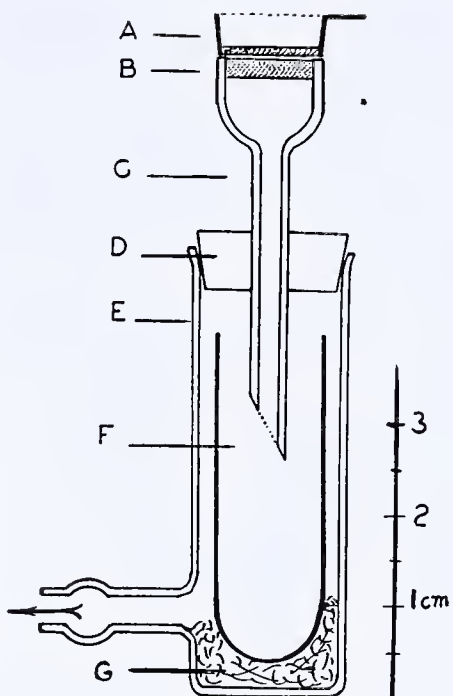


FIGURE 3. FILTERING DEVICE FOR USE WITH MICROPLATINUM FILTER BOAT

- A. Filter boat
- B. Fritted-glass filter disk
- C. Glass filter stick
- D. Rubber stopper
- E. Suction test tube
- F. Microbeaker
- G. Cotton

bottom in the usual manner, as in the preparation of Donau dishes (4). The capacity of the boat is about 0.15 to 0.20 ml. (Figure 3A shows such a filter boat, which is obtainable from the American Platinum Works, Newark, N. J.)

Some advantages of this filter vessel are the following: The sample can be treated with various solvents, cold or hot acids, etc.; the platinum-sponge layer retains barium sulfate precipitates quantitatively; because of the standard dimensions (12  $\times$  5  $\times$  4 mm. high) it can be used in the standard combustion tubes; all the advantages of platinum,

such as constant weight, quick cooling, etc., remain; capillary attraction reduces the tendency of small volumes of liquids to creep over the walls. By means of the filter boat, micropreparative work can be combined directly with quantitative determinations without any change of the vessel—e. g., recrystallizations and isolation of small amounts of crystals, drying, extracting impurities, treatment under varying conditions such as exposure to certain vapors—and finally, the microchemical quantitative analyses can be carried out in one filter boat.

For the filtration, the filter boat is placed on the fritted-glass part of Donau's suction apparatus (4) or on the glass filter stick (No. 91 G 3 of Schott and Genossen, Jena) which has the permanently fused-in fritted-glass filter disk shown in Figure 3B.

I. Determination of Moisture (volatile matter at 105° C.). The air-dried crystals were weighed in the filter boat and heated in a Pregl drying block (8) at 105° C. for 20 minutes to constant weight. All the weighings were carried out with the utmost care under continuous control of the zero readings and the sensitivity of the Kuhlmann microchemical balance. Changes in temperature and moisture content of the balance room were observed and influences of changes in the barometric pressure were eliminated through tares of the same density and similar shape. These precautions were essential for success in working with a 1.3-mg. sample.

II. Analysis of Water-Insoluble Matter. The boat with the dry sample was placed on the filtering device (Figure 3) and treated with 2 ml. of cold water in small portions, allowing each portion to stand in contact with the particles at least 30 seconds before applying suction. The solution was collected in a glass microbeaker. The water-insoluble residue was then dried in the filter boat to constant weight under the same conditions as above.

The small quantity of insoluble material prevented a carbon and hydrogen determination as originally planned; a qualitative analysis was performed instead. A few drops of hot, concentrated sulfuric acid partly dissolved the residue, the filtrate being collected in a 5-ml. platinum crucible. Since it was impossible to tell by visual observation whether complete solution had taken place, the boat was heated on a metal block to drive off the excess of sulfuric acid, and weighed again. It was found that



not all of the residue had dissolved. The remainder was treated with concentrated hydrochloric acid, which finally caused complete solution. The combined acid extracts were concentrated by blowing air on the surface of the heated liquid. The liquid became brown during this treatment, indicating the presence of organic material. After evaporation to dryness, the residue was dissolved in a few drops of dilute hydrochloric acid (1 to 5), and tested by bubbling hydrogen sulfide through the solution from a fine capillary. A positive test for tin was obtained, but no quantitative determination was performed. No other elements of groups 2, 3, or 4 were detected.

The conclusion drawn from these experiments was that the major portion of the water-insoluble material in the crystalline occlusions was tin soap.

III. Analysis of Water-Soluble Matter. The amount of water-soluble material was calculated from the insoluble matter by difference. The water extract was transferred with a fine capillary pipet from the glass microbeaker into a platinum microboat, in which it was evaporated and dried at 110° C. A small amount of material was lost in this procedure, 0.228 mg., as calculated from the difference in the weighings. For the final calculations it was assumed that the lost portion contained the elements in the same proportions as those found in the analysis.

(a) A carbon and hydrogen microdetermination was carried out on the dried sample in the usual manner, but the results had to be corrected because of the noticeable blank tests obtained during the hot summer months as a result of the high humidity and the extremely small amount of sample (organic matter only 0.228 mg.). Comparatively reliable results could be obtained only if "block analyses"—i. e., analyses with about 1.300 mg. of salicylic acid before and after burning the actual sample—established exact corrections for the water and carbon dioxide. The residue consisted of sodium sulfate and sodium chloride, as shown by the good agreement of the total weight (0.795 mg.), as calculated from the chloride and sulfate data, with the actual residue (0.796 mg.).

(b) The residue in the platinum boat was completely soluble in distilled water. To determine chloride, the solution was introduced into a weighed glass microbeaker for the filter-stick method of Emich (6), and the chloride determined by precipitation with silver nitrate.

(c) To determine sulfate, the filtrate from the chloride determination was collected quantitatively in a glass microbeaker, the excess of silver was precipitated with hydrochloric acid, and the silver chloride was filtered off and washed three times with hydrochloric acid (1 to 100). The clear filtrate and the washings were collected in a porcelain crucible with a black glazed inner surface, a type now in general use for barium or sulfate determinations, together with the porcelain filter stick of Emich and Schwarz-Bergkamp (6, 9, 10). The solution had at this point a volume of about 10 ml.; a small portion of it was treated with hydrogen sulfide without noticeable precipitation, and a side test in another drop for group 3 gave negative results. The treated portions were heated on a water bath to remove hydrogen sulfide, combined with the major part of the solution, and the sulfate determination was carried out by precipitating with barium chloride crystals.

(d) To determine sodium, the filtrate from the sulfate determination was collected in a glass beaker and the excess of barium

removed with sulfuric acid (1 to 5). After filtering off the barium sulfate by means of a porcelain filter stick, the solution was evaporated in a platinum microboat on a water bath, and the sodium determined as sodium sulfate in Pregl's micromuffle (8). The sodium sulfate dissolved completely in water, and the solution gave no tests for group 4 or other elements of group 5.

From the results reported in Table III, the complete analysis (Table IV) could be calculated. For the calculation it was necessary to assume that the water-insoluble material was pure tin soap.

TABLE IV. CALCULATED ANALYSIS

Determination	Per Cent Found	Calculated from:
Moisture	3.5	Volatile matter, I
Tin soap	5.5	Water-insoluble matter, II
Organic matter (sodium soap and free fatty acids)	20.3	Carbon and hydrogen, loss of weight on burning, III a (organic part of tin soap not included)
Sodium chloride	2.0	Chloride determination, III b
Sodium sulfate	68.7	Sulfate determination, III c
Total	100.0 <sup>a</sup>	

<sup>a</sup> The 100.0% yield should not be considered as an indication of such high accuracy.

## Conclusion

The main constituent of the crystalline occlusions in the soap bars was determined to be sodium sulfate. Because of the small moisture content the sodium sulfate was almost dehydrated. The tin soap was present in a higher concentration than in the soap without crystals and may be tied up with the formation of the crystals. The chloride content was comparatively small. The sodium soap was calculated from the organic matter in the water-soluble part of the crystals and was not considered as a constituent of the crystals. Quantitative mechanical separation of the dendritic crystals from the soap was nearly impossible.

## Summary

The application of microchemical methods in industrial problems is illustrated by the analysis of heterogeneous particles in soap bars. In the two cases described, the use of microtechnic enabled explanations to be given for the appearance of troublesome disturbances during the process of manufacturing soap; attempts to apply macrotechnic to these problems had failed. The use of "classical micromethods" is emphasized; modifications were made only when the extremely small amounts of material at hand demanded them. A new microplatinum filter boat is described which permitted seven successful quantitative determinations to be carried out on a single sample weighing 1.3 mg.

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TABLE III. QUANTITATIVE ANALYSIS

No.	Type of Determination	Weight of Sample	Reaction Products Determined as	Found
		Mg.	Mg.	%
I	Volatile matter at 105° C.	1.376	Loss in weight	0.048 3.5
II	Water-insoluble matter	1.328	Residue insol. in water	0.076 5.7
II a	Qualitative analysis of II	0.076	Organic material and tin, probably in form of tin soap. Groups 2, 3, and 4 = —	5.5 <sup>a</sup>
III	Water-soluble matter	1.328	Water extract, calcd. from II	1.252 94.3
III a <sup>b</sup>	Carbon	1.024	CO <sub>2</sub>	0.575 15.3
	Hydrogen	1.024	H <sub>2</sub> O	0.275 3.0
	Residue in III	1.024	Residue	0.796 77.7 (70.7 <sup>a</sup> )
III b	Chloride in residue from III a	0.796	AgCl	0.055 1.7 (1.2 <sup>a</sup> )
III c	Sulfate in residue from III a	0.796	BaSO <sub>4</sub>	1.27 65.7 (46.4 <sup>a</sup> )
III d	Sodium in residue from III a	0.796	Na <sub>2</sub> SO <sub>4</sub>	0.881 35.8 (25.3 <sup>a</sup> )

<sup>a</sup> Values calculated on basis of air-dry sample (original crystals).

<sup>b</sup> Refers to the previous remark concerning loss of material (0.228 mg.).



# Microdetermination of Carbon and Hydrogen

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**I**N THE past few years several papers have appeared (3, 5, 6, 8) dealing with personal experiences in the field of microanalytical chemistry. Such exchanges of information are valuable and illuminating and often promote the development of new ideas. In the course of many thousands of organic and inorganic microanalyses during the past 12 years, several unpublished modifications of the original Pregl technic have been devised in this laboratory. Much of the experience derived from 8 years of organic and inorganic macroanalytical work was found to be more or less directly applicable to the newer micromethods, and bears out the contention that a thorough competence in macroanalysis is advantageous for success in microanalysis. The laboratories of the Rockefeller Institute for Medical Research were among the first in this country to realize the importance of Pregl's methods and to perform microanalyses (6).

## Balance

For all the microanalyses made by the author a single Kuhlmann microchemical balance has been employed with complete satisfaction, and beyond periodic cleaning by the sole user has never required any repair. It is kept in a glass house (locked after working hours) and adequate precautions are taken to reduce vibration to a minimum. When in use, the zero point is adjusted before commencing weighing instead of calculating the results with a shifted zero point. The same zero point must be maintained throughout any single determination. Tiedcke (8), among others, has stressed this point.

## The Combustion Train

The usual Pregl pressure regulator is used. A large U-tube is inserted at its distal end; to absorb traces of carbon dioxide and moisture and to protect the bubble counter, it is filled with Ascarite and "indicating" Drierite. Drierite is more convenient than calcium chloride, phosphorus pentoxide, or Anhydrone because the distinct color change readily shows the condition of the absorbent, while it does not deliquesce like hydrated calcium chloride, which often blocks the passage of gas. It can be used to the last granule and does not have to be preheated. The combustion tube employed is equipped with a side arm and is made of Supremax glass as described by Pregl (7). The tube filling follows the recommendations of Pregl, except that it has been found advantageous to use a fine-meshed, pure silver gauze instead of silver thread. This is cut to appropriate length and rolled tightly until it is sufficiently thick to fit snugly inside the combustion tube. It is reduced in hydrogen in the usual manner before use. The silver gauze has a larger surface area and is also easier to handle.

Since 1926 a simple electric heater made in this laboratory has been used instead of the long gas burner. It consists of an aluminum tube (7 inches long and 0.625 inch inside diameter) on which is wound Nichrome wire. (That part of the combustion tube which is within the heating unit is wrapped with asbestos paper.) Around it is alundum cement, then asbestos paper, both cement and asbestos being thick enough to prevent the radiation of heat. This heater is connected through a rheostat to regulate the temperature (between 650° and 700° C.). Alongside the combustion tube within the heater lies a thermocouple which is connected to a pyrometer. Recently, however, the heater has been equipped with a pyrometer and automatic control unit. The electric heater ensures a uniform temperature all around the tube without distorting it throughout its life, which was not true of the gas burner. For the combustion of the sample a gas burner is

**Experiences in the microdetermination of carbon and hydrogen with suggestions and modifications as to method and technic are described. The technic using two boats and two capillaries has contributed to the accuracy of carbon and hydrogen determinations for easily subliming or volatile substances.**

used because its greater flexibility permits ready adjustment for the conditions imposed by its nature. The regular heating mortar, containing decahydronaphthalene, is used to keep the temperature of the lead peroxide at about 190° C. This arrangement has also been recommended by Roth (7).

The furnace is connected through a clock-controlled switch, which automatically starts it at any set time and maintains operation for any desirable period of time. If the set time is properly chosen, the combustion train will be ready for use when the analyst commences to work; the heating of the furnace can be discontinued on nonworking days.

## Absorption Tubes

Much has been done in attempts to develop a satisfactory technic for the manipulation of absorption tubes. The experiences in this laboratory support the findings of Hayman (1) and Hernler (2) concerning the importance of keeping the humidity about 50 per cent to dispel static charges. Other factors enter to a greater or lesser extent, however. Not the least of these is the differing susceptibility of various types of glass. Many different glasses were tried; the most suitable was Jena thermometer glass. By using tubes made of this glass, and as a further safeguard by grounding the balance, difficulties arising from static charges were satisfactorily eliminated. Naturally, the absorption tubes must be cleaned and handled meticulously. The capillary ends of the absorption tubes are made from special uniform-bore (0.2-mm.) capillary tubing and then sealed to the body of the tubes. This ensures greater regularity than is practicably attainable when the ends are drawn out from the body of the tube in the usual manner.

## Oxygen

It has been a general complaint that the figures obtained for hydrogen are often too high—sometimes as much as 0.5 per cent. Early experience with macrocombustions showed that this condition could be traced to varying amounts of hydrogen in the oxygen drawn from the cylinders. The oxygen had been prepared by electrolysis, and the hydrogen present as impurity was presumably derived from incomplete separation of the gases at the electrodes. By using oxygen manufactured from liquid air this difficulty was readily overcome in macrocombustions and, carrying over this experience into the microtechnic, high hydrogen results have not been encountered in this laboratory. The small amount of nitrogen present as impurity in liquid-air oxygen is unimportant. It is, however, important to possess personal cylinders which are never to be used for the storage of electrolytic oxygen. The less experienced must naturally learn to insert the sample into the combustion tube with the minimum of time in order to avoid exposing the tube unduly to the room air.

## Methods and Technic

**TECHNIC OF THE TWO BOATS.** Substances which sublime readily must be burned very slowly with a small flame located 3 to 4 cm. away from the boat. On one occasion, a pyrazine derivative sublimed so readily and traveled through the tube so rapidly that, even with the greatest precautions, the com-



bustion was incomplete and the value obtained for carbon was low. There had been reported in the literature (4) just such difficulties with this type of compound. The following procedure has been utilized to solve them:

The substance is weighed in an ordinary platinum boat and sprinkled with fine, previously heated copper oxide. Another, somewhat smaller, platinum boat is inserted into the former, so that the handles are at opposite poles. By conducting the combustion slowly, accurate results have been obtained with such compounds. This arrangement has been termed the "technic of the two boats."

**TECHNIC OF THE TWO CAPILLARIES.** During the last few years several thousand samples of organic liquids, having a large variety of structure, have been analyzed. Some could be burned in the usual way, while others were very volatile. The following procedure has proved useful:

The sample is weighed in a regular capillary. The tip is broken off and the capillary is placed in another somewhat larger capillary about 1 cm. long which is closed at one end. The larger capillary is filled with copper oxide or, if the substance is a halide, with precipitated and previously dried silver. These two capillaries are placed in a suitable long platinum vessel. This arrangement has been termed the "technic of the two capillaries."

Certain organic halides (especially bromides and iodides) containing a high percentage of halogen yielded rather high values for carbon despite the rolls of silver gauze in the combustion tube. The additional silver placed in the larger of two capillaries by means of the technic described above absorbs most of the halogen and lengthens the life of the silver gauze. The two capillary arrangements also diminish the speed of vaporization of the volatile liquid sample; hence a more complete combustion can be expected.

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# Turbidimetric Titration of Small Amounts of Nicotine

## By the Use of a Photoelectric Cell

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An inexpensive photoelectric apparatus, including a special titration cell, is used for the turbidimetric titration of small amounts of nicotine. The unknown nicotine sample is added to an excess of silicotungstic acid and the excess of the latter is titrated with standard nicotine formate. Results that check to about 5 micrograms can be obtained. Flocculation of the precipitate is prevented by the addition of Irish moss extract, and the tendency to crystallize is retarded by using formic acid instead of hydrochloric acid as in the analysis by the gravimetric method.

CERTAIN fumigation and dusting experiments in progress at the laboratory of the Division of Insecticide Investigations required a rapid method for the determination of small quantities of nicotine. A survey of the numerous available methods, which include gravimetric, nephelometric, and colorimetric procedures, did not reveal a method of analysis without objection in one respect or another. Although not previously reported for nicotine, titration to maximum turbidity appeared to be a rapid and accurate method, if certain conditions, such as very low solubility and stabilization of the precipitate, could be realized.

The use of the photoelectric cell to indicate the point of

maximum turbidity during the titration of  $\text{SO}_4^{--}$  with  $\text{Ba}^{++}$  was recently suggested by del Campo, Burriel, and Escolar (1). Large volumes (200 cc.) were used, however, and, since stabilization of the precipitate was not complete, a continuous stirring device was necessary. No details regarding the apparatus or the type of photoelectric cell were given.

### Experimental

In the turbidimetric titration of nicotine with silicotungstic acid, it was found that more accurate results were obtained when the nicotine solution was added to the silicotungstic acid than when the reverse procedure was used. A definite quantity of silicotungstic acid in excess of the unknown nicotine sample was placed in the titration cell and the excess titrated with standard nicotine solution. The quantity of nicotine solution equivalent to the silicotungstic acid was determined by a blank titration. The end point of the titration was obtained by plotting the scale readings of the photoelectric apparatus against cubic centimeters of standard nicotine.

**DESCRIPTION OF APPARATUS.** The circuit shown in Figure 1 employs a highly sensitive gas-filled photoelectric cell, 918, with one power amplifier, 1F4. Because of its instability, a gas-filled cell is not usually recommended for an instrument of this kind, but if a separate battery is used to supply the potential across the photoelectric cell, and the grid of the amplifier is connected with the anode, a nearly constant plate current is obtained. In this way the effects caused by the small changes in resistance of the vacuum tube and the photoelectric cell practically neutralize each other.

The over-all sensitivity of the set can be varied within wide limits by varying the load resistance,  $R_1$ . About 40 megohms have been found to give good sensitivity without sacrificing stability. The sensitivity can be increased by using an indicator,



MA, with a range of 1 milliampere in connection with a compensating current so that only the change in the plate current is measured. Variable resistors,  $R_2$  and  $R_3$ , are used to adjust the indicator on the scale and to return it to zero after the scale has been traversed once. A 10-to-1 shunt,  $R_4$ , can be used to protect the milliammeter when necessary. Also, in this circuit the greatest sensitivity is obtained when the screen grid and the plate of the vacuum tube are connected and operated at 90 volts.

A constant source of light is obtained from a 60-milliamperere radio pilot light,  $L$ , operated by a 2-volt storage cell. About 1 per cent of the light from the filament is utilized. This small amount will change the plate current 10 milliamperes.

The design of the apparatus may be adapted to the needs of the individual. The author has found it convenient to use a steel cabinet 20 × 30 × 17.5 cm. (8 by 12 by 7 inches). All instruments are mounted on a Bakelite panel, which is dropped 2.5 cm. (1 inch) below the top of the cabinet to allow the lid to be closed when the set is not in use.

The titration cell shown in Figure 1 is made by welding a portion of a small (12-mm.) inverted test tube in the bottom of a larger (25-mm.) test tube. This indentation accommodates the small pilot light. As little as 5 cc. or as much as 40 cc. can be titrated. The heating effect of the light is so slight that no perceptible rise in temperature is noted for an hour or more.

A holder for the titration cell consists of a brass tube mounted below the panel 6.5 cm. (2.5 inches) from the photoelectric cell. The light is held at the lower end while the upper end opens above the panel. A 4-mm. hole in the side of the brass tube opposite the filament allows more than enough light to fall on the photoelectric cell. A black paper on the photoelectric cell in which a small opening is cut serves to reduce the light further and to exclude radiation and reflection from the vacuum tube.

A set of this type should be protected from the capacity effects of the operator by a shield under the panel over the vacuum tube and photoelectric cell. The grid lead should be very short. Some kind of spring socket should be used for the vacuum tube, since a sharp jar may change the position of the elements slightly and ruin a determination.

A 5-cc. microburet graduated to 0.02 cc. is used in the titrations, and is held by a removable stand built into the panel of the apparatus. Only pipets having a delivery that varies less than 0.005 cc. from the indicated volume are used. A stirrer for use with the titration cell is made by bending the end of a glass rod into a nearly complete circle in a plane perpendicular to the rod. The opening in the circle is held in such a position that the stirring motion does not interrupt the beam of light falling on the photoelectric cell.

REAGENTS. A silicotungstic acid solution made by dissolving 5 grams of silicotungstic acid ( $4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 22H_2O$ ) in 1 liter of water. (Three samples of silicotungstic acid were tried, but no significant difference in the results was noted.) The turbidity is removed by settling and decanting.

A standard nicotine formate solution made by adding enough formic acid to neutralize both basic groups in 0.5 gram of nicotine and diluting to 1 liter. The exact amount of nicotine was determined by the official A. O. A. C. gravimetric method. This solution is stable for at least 2 months. This concentration ap-

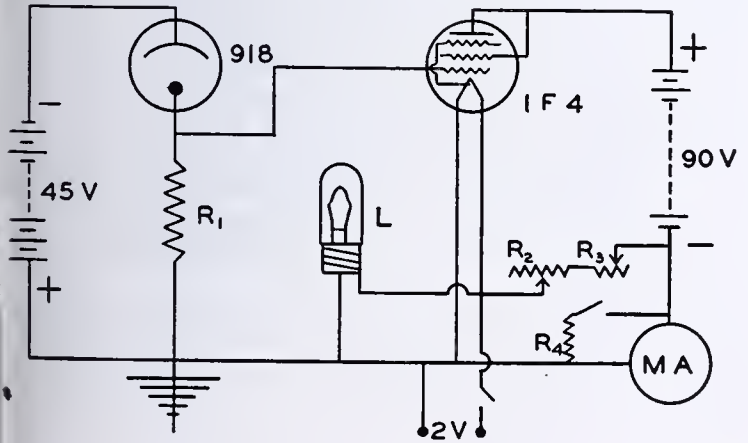


FIGURE 1. WIRING DIAGRAM AND TITRATION CELL

- $R_1$ , 40-megohm load resistance
- $R_2$ , 2000-ohm radio potentiometer
- $R_3$ , 200-ohm radio potentiometer
- $R_4$ , one-tenth the resistance of milliammeter
- MA, milliammeter with 0 to 1 range
- L, 60-milliamperere, 2-volt light
- 918, sensitive gas-filled photoelectric cell
- 1F4, power amplifier with high amplification factor

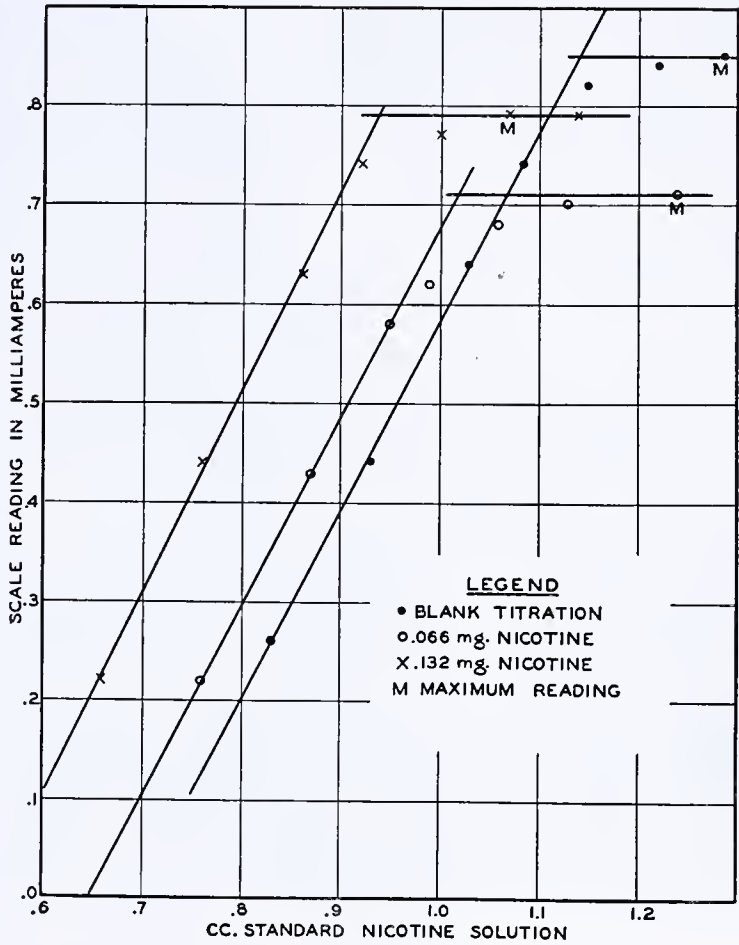


FIGURE 2. TITRATION CURVES, SHOWING METHOD OF LOCATING END POINT

Two or three points at maximum turbidity are always noted. Some points are too far to the right to be included on this graph.

pears to be the optimum for the most precise results with this apparatus.

A 1.5 M formic acid solution. An extract of Irish moss made by soaking 2 grams in 200 cc. of water overnight, decanting, washing, and boiling 30 minutes in 100 cc. of water. The cellular material was strained out with cheesecloth but not pressed, because this increases the turbidity of the extract. A crystal of thymol must be added to prevent the growth of mold. This solution is stable for a month or more.

General Procedure

For samples of from 0.05 to 0.75 mg. of nicotine, 2 cc. of the silicotungstic acid solution are pipetted into the titration cell, and 4 drops of the formic acid solution, 4 drops of Irish moss extract, and 10 cc. of water are added. The cell is placed in the apparatus, the indicator adjusted to zero, and titration made with the standard nicotine solution. After about half the titration has been done, readings should be taken about every 0.1 cc. The contents of the cell must be well stirred after each addition and about 30 seconds allowed for complete precipitation. The titration is continued until the maximum reading remains constant for 0.2 to 0.3 cc., after which a small dilution effect becomes apparent. To determine the end point the scale reading in milliamperes is plotted against cubic centimeters of standard nicotine (Figure 2). A straight line is obtained over the last one-third to one-half of the titration up to within less than 0.1 cc. of the end point. The end point is taken as the intersection of this projected line with a horizontal line passing through the point of maximum turbidity.

For the analysis of an unknown sample of nicotine, which should be contained in dilute formic acid solution, the same procedure should be carried out, except for the substitution of the unknown nicotine solution for a portion of the water.



TABLE I. TITRATION OF NICOTINE BY THE TURBIDIMETRIC METHOD

Nicotine Solution Taken Cc.	Nicotine Taken Gram	Silicotungstic Acid Taken Cc.	Titration Cc.	Nicotine Found Gram	Nicotine Solution Taken Cc.	Nicotine Taken Gram	Silicotungstic Acid Taken Cc.	Titration Cc.	Nicotine Found Gram
0.0	0.0	1	1.14	...	0.5	0.066	1	1.01	0.075
...	...	.	1.145	...	...	...	.	1.02	...
...	...	.	1.15	...	...	...	.	Av. 1.015	...
...	...	.	1.14	...	1.0	0.132	1	0.935	0.127
...	...	.	1.155	...	...	...	.	0.920	...
...	...	.	1.16	...	...	...	.	0.935	...
...	...	.	1.15	...	...	...	.	0.915	...
...	...	.	1.13	...	...	...	.	Av. 0.926	...
...	...	.	1.14	...	2.0	0.263	1	0.68	0.268
...	...	.	Av. 1.145	...	...	...	.	0.695	...
0.0	0.0	2	2.28	...	...	...	.	0.675	...
...	...	.	2.27	...	...	...	.	Av. 0.683	...
...	...	.	2.29	...	5.0	0.659	2	1.14	0.660
...	...	.	2.29	...	...	...	.	1.14	...
...	...	.	2.27	...	...	...	.	Av. 1.140	...
...	...	.	2.26	...	...	...	.		
...	...	.	Av. 2.277	...					

The same volume in the titration cell should be reached at the end point of each titration. The difference in the two titrations multiplied by the concentration (milligrams per cubic centimeter) of nicotine in the standard solution gives the nicotine in the unknown sample. Duplicate determinations should be run on both the blank and the unknown. The blank titration remains constant from day to day and serves as a check on the apparatus. The titration cell must be washed with dilute sodium hydroxide at least once a day to remove any seed crystals that might form on the walls of the container.

### Results

To test the accuracy of the method a known solution of nicotine was used. By gravimetric analysis it was found to contain 0.1318 mg. per cc. The gravimetric analysis of the standard nicotine solution on two different days showed 0.5802 and 0.5795 mg. per cc. For the smaller amounts of nicotine only 1 cc. of silicotungstic acid was used in half the 12-cc. volume indicated above. A summary of the titrations and a comparison of the results with those obtained by gravimetric analysis are given in Table I.

### Discussion of Method and Results

The precision of the method depends primarily on how accurately the end point can be determined. About 0.01 cc., which is equivalent to 0.0058 mg. of nicotine, seems to be the lower limit. The average of several volumetric determinations appears to check the gravimetric results with about the same precision.

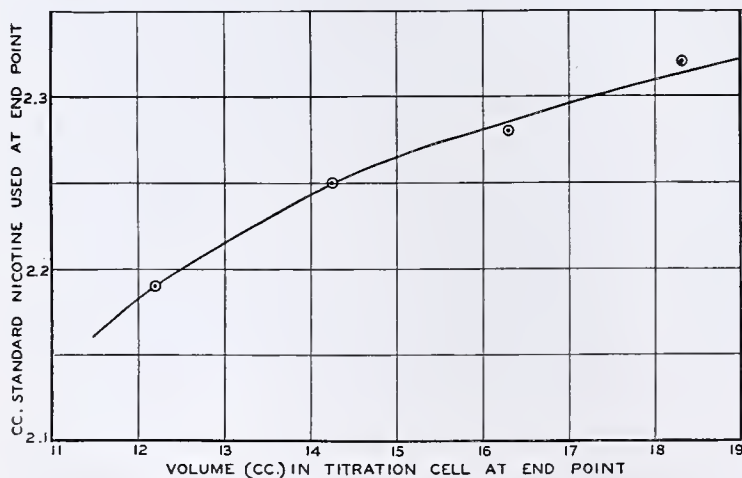


FIGURE 3. EFFECT OF VOLUME ON END POINT

Two cubic centimeters (10 mg.) of silicotungstic acid were titrated in four different total volumes. The relationship shown is equivalent to a rectilinear variation of titer with concentration of silicotungstic acid.

The final volume affects the end point of the titration. This effect has been determined by titrating 2 cc. (10 mg.) of silicotungstic acid in four different volumes. The results are presented graphically in Figure 3. If the volume at the end point is constant to 5 per cent, very little effect will be noted. To increase the accuracy, a correction can be read from the curve and applied or a second aliquot can be titrated in which the exact volume of water is used. The results recorded in Table I were obtained with volumes constant to 2 per cent.

The concentration of formic acid was varied from 0.01 to 0.03 *M* without affecting the end point. At concentrations below 0.01 *M* the end point was indefinite. Concentrations above 0.03 *M* were not investigated, but it is known that the precipitate is more soluble with increasing concentration of acid. Hydrochloric acid cannot be used, because it promotes the formation of large crystals. Acetic acid was tried, but it apparently exerts a solvent action on the precipitate of nicotine silicotungstate.

Among the stabilizers tried were agar-agar, gum karaya, gum tragacanth, gum arabic, saponin, gelatin, and Irish moss extract. Irish moss was the only one that gave any protection. A very small amount of this will prevent flocculation for several days.

The equipment required for a microdetermination of this type is inexpensive. A photoelectric apparatus such as the one described above can be built in any laboratory for about \$25. No expense need be added for the titration cell, since it can easily be made where glass-blowing equipment is available.

For the analysis of small quantities of nicotine, this turbidimetric titration appears to be a rapid and accurate method. It eliminates errors due to solubility of the precipitate and avoids an indefinite end point. For extremely accurate results the Spies gravimetric method (2) is preferable, but where a large number of analyses must be run and results to 5 or 6 micrograms are sufficiently accurate, this method has many advantages.

This method of titration appears to be applicable in the determination of other substances whenever a good precipitation reaction can be found. Experimental work on its application to the analysis of other materials is in progress.

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# Drying and Weighing Hygroscopic Substances in Microanalysis

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Methods for drying and weighing hygroscopic substances are described, stressing the necessity of determining the relative hygroscopicity of every sample submitted for analysis. A microbalance, capable of giving readings constant to  $\pm 0.002$  mg. over a period of several minutes, is essential for this determination.

A new type of pig is described and a special technic which makes it possible to weigh the sample and pig to  $\pm 0.002$  mg.

THE degree of hygroscopicity of samples is one of the first properties that must be determined by a microanalyst. Hygroscopic materials must be handled in such a way that their tendency to pick up water does not interfere with the correctness of the weighing. The degree of hygroscopicity varies from one barely noticeable to so fast an addition of water of hydration that it is detected (1, 2) only by special observation. The microbalance used to make these determinations of relative hygroscopicity on routine samples must be highly constant: The observed weight of a non-volatile, nonhygroscopic substance should not vary by more than  $\pm 0.002$  mg. over a period of several minutes.

The method used in handling the sample should be determined by the relative hygroscopicity of the material.

## Carbon and Hydrogen Determinations

It is customary in routine analyses of carbon and hydrogen to weigh the sample during the free period following the actual combustion while the combustion tube is being swept out. If the material shows any sign of hygroscopicity, the sample should not be weighed until just before it is placed in the combustion tube. A constant balance is essential to detect this type of compound.

When the weight increase is no greater than 0.001 mg. per swing of the pointer, fast weighing followed by immediate introduction of the sample into the combustion tube gives excellent results. It is not necessary to swing the pointer of a good balance more than three times to obtain an accurate weighing. The total time of handling can be determined and correction can be made for the pickup over this period of time when the total amount of water absorbed is between the limits of 0.004 and 0.020 mg. When the total correction is above 0.020 mg., it is advisable to protect the sample from moisture. The method, recommended by Pregl (4), of placing the sample in a large glass "pig" is acceptable only for a small proportion of moderately hygroscopic substances. Various other methods of handling hygroscopic samples for carbon and hydrogen have been proposed (1, 2, 3, 5). While all these methods have advantages, they have certain limitations. The new methods to be described have proved useful in many cases, but do not solve all the difficulties encountered in handling hygroscopic materials.

The apparatus shown in Figure 1 (the pig) was developed for the type of compound which absorbs water at the rate of 0.001 to 0.010 mg. per swing of the pointer. This pig was made as small as possible in order to permit the inclusion of a

Used with a copper boat, the special pig has also proved useful for the determination of nitrogen by the Dumas method.

A revised method is given for handling substances which must never come in contact with damp air. Two samples are dried in the combustion tube: one of about 3 mg., the other of 15 to 20 mg. The water is determined on the larger sample, while the actual combustion is made on the smaller sample.

standard size platinum boat, except that its length was cut to 7.5 mm. By using an inner ground cap, rather than the outer ground stopper used in the Pregl type of pig, the weight may easily be held to 1 gram, whereas the Pregl type weighs from 3 to 4 grams.

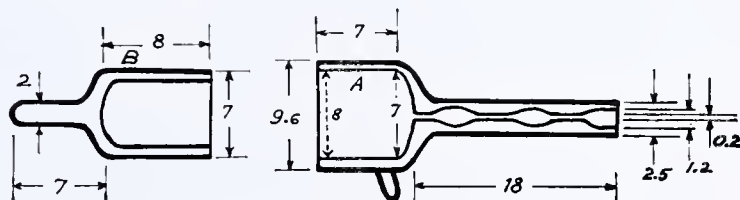


FIGURE 1. DIAGRAM OF APPARATUS

A, B. Ground surfaces  
(Dimensions in mm.)

The size of the pig is important for two reasons: (1) the weight should be as low as possible to cut down the amount of glass to be weighed, and (2) the surface of glass must be as small as possible in order to reduce error caused by temperature change, humidity change, static charge on the surface, dust and lint collection, or handling error.

The tip was made like the tip of a Pregl absorption tube with two long capillaries 0.2 mm. in diameter. The pig had wide-spread feet, so that it was not easily upset. A good grade of soft glass was used which was not susceptible to static charge.

Since the glass pig was weighed to  $\pm 0.002$ -mg. accuracy, a special technic of handling was necessary. Once the pig was clean, it was never touched with the hands but only with platinum-tipped tweezers. Before weighing, it was always allowed to come to constant temperature near the balance.

The clean pig and platinum boat, both of which had been resting near the balance, were placed on the balance pan, counterpoised by glass, and then weighed. The glass surface was never wiped but was carefully stroked with a soft camel's-hair brush. The previously dried sample was placed in the platinum boat, this in turn was put in the pig, and the pig was placed in a tube similar to an Abderhalden dryer, with attachment for a vacuum connection. In many cases the samples were dried under high vacuum without heat or, if necessary, were heated in the Abderhalden dryer. The whole tube was removed to the balance room after drying and allowing to cool on a metal block. Cool, dry air was then admitted slowly and the pig was removed, placed on a metal block near the balance for 3 minutes, and then weighed. The whole pig was removed to the combustion tube into which the boat was quickly introduced.

Certain hydrates gave the correct amount of water by drying with heat, yet could never be transferred to a combustion tube and analyzed, since the water was taken up almost instantly. This unusual degree of hygroscopicity



has been described before (1, 2). The method previously given by the author (1) has been improved and consists in drying two weighed samples simultaneously in the regular combustion tube with heat from a Pregl drying block, and with a current of nitrogen passing through the tube. The first boat contains the sample for combustion, the next boat a sample weighing 15 to 20 mg. The water driven off can be determined with much greater accuracy than by the previous method. Before combustion the larger sample is removed and a carbon-hydrogen determination is made on the smaller sample, the weight of which has been corrected for its share of loss of weight on drying.

### Determinations by the Dumas Method

The special pig has been used without an inner boat for certain lumpy solids, but it has been found more convenient to weigh the material in a copper boat, which later is introduced into the combustion tube eliminating the use of a shaking bottle when the samples have a tendency to stick to the walls.

### Summary

Methods which have given satisfactory results for drying and weighing hygroscopic substances stress: (1) the neces-

sity of a microbalance giving readings constant to  $\pm 0.002$  mg. over a period of several minutes, (2) determination of the relative hygroscopicity of a substance to find the best method of handling and weighing, (3) a new type of pig and a special technic which makes it possible to weigh the sample and pig to  $\pm 0.002$  mg., (4) a revised method of handling substances which must not come in contact with the moist air even for an instant, and (5) the use of the special pig in conjunction with a copper boat for the determination of nitrogen by the Dumas method.

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## Weighing Tube for Volatile Liquids in Carbon-Hydrogen and Dumas Nitrogen Semimicrodeterminations

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IN THE micro- and semimicrodetermination of carbon-hydrogen and Dumas nitrogen according to Pregl (1), volatile liquids are weighed in glass capillaries containing a few crystals of potassium chlorate at one end and drawn down and sealed at the other (Figure 1).

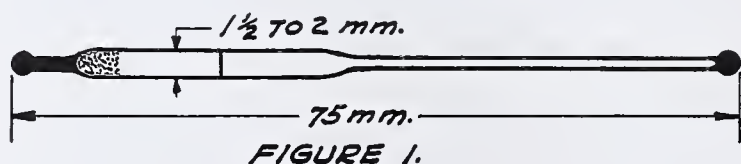


FIGURE 1.

The U-shaped design shown in Figure 2 has been found more convenient for these determinations. By avoiding the use of potassium chlorate the filling of the capillary is simplified and the sample is expelled much more smoothly. One capillary end is longer than the other to facilitate handling; the other end is sealed.

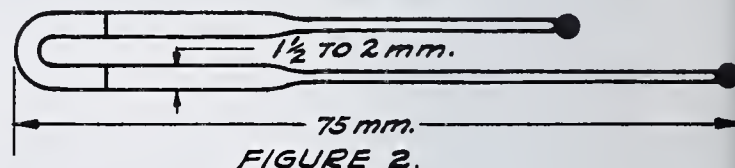


FIGURE 2.

When carrying out a determination the tube is weighed, filled as usual by warming in a flame, and cooled with the long end dipping into the sample contained in a 1-cc. beaker. After centrifuging briefly to force the sample into the bend of the capillary, the end is sealed and the tube is reweighed. Both ends are then broken off; the tube is placed in a porcelain boat and promptly introduced into the combustion tube with the open ends slightly elevated and facing the furnace.

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RECEIVED October 29, 1937.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION

Harrison E. Howe, Editor

## Preparation and Testing of Latex Compounds

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WHILE the American Society for Testing Materials has standardized the conditions for the testing of crude rubber (1) compounds, there are no such accepted standards for testing latex compounds. Wohler (7) outlined the first constructive ideas on this subject. The object of this paper is to continue the work started by Wohler (7) and to suggest simple methods which will give reproducible results. Since latex is a variable material in itself and presents numerous difficulties in testing, it is necessary to employ certain precautions in the testing procedure which will be outlined below.

TABLE I. TYPICAL LATEX FORMULA

	Dry Basis	Wet Basis
Rubber as 60% centrifuged latex	100.0	166.6
Zinc oxide as a 50% dispersion	1.0	2.0
Sulfur as a 50% dispersion	1.5	3.0
Piperidine cyclopentamethylene dithiocarbamate (Pip-Pip)	0.5	0.5
Water to 54% total solid content	...	18.9

In Table I is given a typical latex formula which is employed throughout this paper with the one exception noted below. The zinc oxide and sulfur are added as aqueous dispersions, and the piperidine cyclopentamethylene dithiocarbamate as an aqueous solution. This formula was chosen on account of its simplicity and to eliminate as many variables as possible.

### Preparation of Latex Test Films

The preparation of smooth uniform latex test films is necessary to obtain reliable results. It is generally customary to prepare the test films by: drying on glass trays in an oven at 45° C. (3), on unglazed tile at room temperature (5), or on glass trays at room temperature (7). These methods were not used here because the glass trays are difficult to clean; the use of the oven is impractical when comparing a series of compounds and may also cause prevulcanization at 45° C.; and the unglazed tile will remove water-solubles and will not produce a smooth surface on the film adjacent to the tile. Experiments proved that ordinary plane glass surfaces were satisfactory and much easier to prepare, the surface tension of any latex compound being sufficient to prevent its flowing over the edges, if the film is not too thick and there are no large chips around the edges of the glass surface.

Therefore, ordinary window-glass plates 25.4 × 33 cm. (10 × 13 inches) are employed. These glass plates are placed on racks (Figure 1), leveled by means of screws, and protected from air

A simplified method for obtaining uniform and reproducible physical test data on latex compounds is described. The control of temperature and humidity from the pouring of the films to the ultimate testing of the test strip is necessary to produce these results.

currents by sheets of heavy single-nap cotton sheeting supported on a wood framework, forming a hood or chamber. A similar method has been suggested by Flint and Naunton (4).

The compound shown in Table I is allowed to stand about 1 hour to permit the escape of air bubbles, the foam is removed, and the compound is then stirred carefully to prevent possible stratification.

Wohler's (7) use of burets was not followed because of their inconvenience and possibility of stratification; 250-cc. beakers were substituted. Two layers of fine cheesecloth (about 36 threads per inch, 14 threads per cm.) are fitted into the beakers, about 225 cc. of the compound are poured into this cheesecloth, and the cheesecloth is removed by withdrawing upward and over the side of the beaker, thus removing foreign material and breaking up all residual air bubbles. The 225 cc. of latex compound are poured on the glass plates, giving a dry film 1.52 mm. (0.060 inch) thick. Care must be taken to avoid all air currents during the pouring and first 8 hours of drying. During this first drying period the relative humidity must be maintained at 60 to 70 per cent and the temperature must not be permitted to go below 21.2° C. (70° F.); after 8 hours the films have set sufficiently (although they may contain 15 per cent moisture) so as not to be affected by external conditions. The chamber is then opened for the free circulation of air to complete the drying process. In approximately another 8 hours the films have dried to a uniform color, which may be taken as an end point, and are removed from the glass plates and suspended to dry at room temperature.



FIGURE 1

The elimination of all air currents is essential from the time of pouring the film to the end of the setting period; otherwise a wrinkled surface will be obtained. Relative humidities below 60 per cent cause the formation of a surface skin over the wet film, resulting in deep surface cracks. Temperatures below 21.2° C. (70° F.) require a prolonged setting period and may result in the formation of wrinkles.

The absolute elimination of moisture in the uncured film is necessary to prevent retardation in air cures, but the presence



of small percentages of moisture in the uncured film does not affect hot water cures. The drying period before cure should not be greater than 48 hours, as shown in Table II.

TABLE II. TESTS ON UNCURED FILM

Drying at 26.6° C. (80° F.)	2 Days		5 Days		9 Days	
	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.
Modulus at 500%	20.4	290	26.7	380	32.3	460
Modulus at 700%	62.5	890	78.8	1100	103.3	1470
Tensile at break	128.0	1820	151.3	2150	225.0	3200
Elongation at break, %	870		860		880	

The dried films are each divided into six sections of  $7.35 \times 13.97$  cm. ( $3.25 \times 5.5$  inches) in order to obtain a range of cures, and the balance of the film is kept to determine the degree of prevulcanization at the time of testing. The curing of these films can be carried out at any desired temperature or time. The usual procedure with this compound is to carry out cures for 0, 5, 10, 15, 20, 30, and 50 minutes in water at 100° C., or for 0, 10, 20, 30, 50, 90, and 130 minutes in air at 85° C. The films cured in water at 100° C. must be dried at room temperature for about 24 hours to allow them to shrink to a minimum thickness and the hot air-cured films are placed in a desiccator for about 24 hours to prevent their adsorbing moisture from the atmosphere.

The preparation of the latex test pieces is carried out in the manner outlined by the American Society for Testing Materials (1). The die for the preparation of the test pieces must have perfect cutting edges (4), giving a clean cut; otherwise short breaks and variable tensiles and elongations will be obtained. This is more evident in essentially pure-gum stocks than in stocks containing even 5 per cent filler on the rubber. In order to accomplish this, one die must be used only for pure-gum latex stocks, and this die should be sharpened frequently with a fine stone or razor hone.

The conditioning of the test pieces is markedly more important when testing latex compounds than when testing crude rubber compounds. Wohler (7) recognized the absolute necessity of controlling the humidity during the conditioning for testing of latex test pieces. Figure 2 shows a photograph of the device used for controlling the humidity for conditioning the test strips.

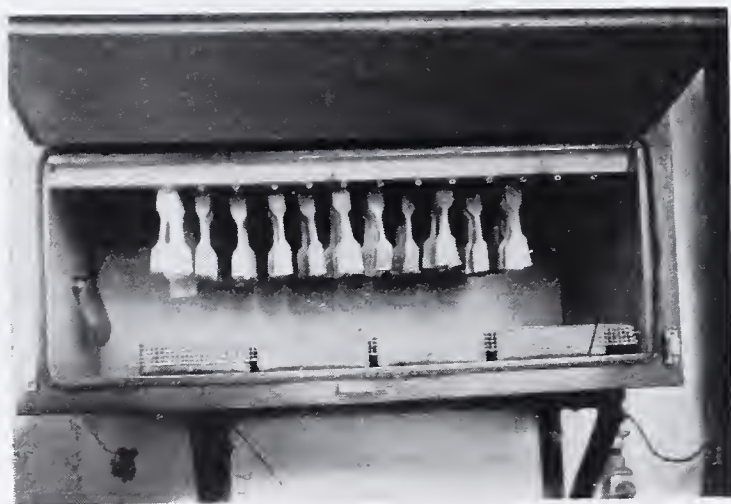


FIGURE 2

Holes are punched in the end of the test pieces which are suspended on a steel wire, the wires being held in the cabinet by hooks attached to its upper framework. Lead trays 3.81 cm. (1.5 inches) deep containing concentrated sulfuric acid (100 per cent) fill the bottom as completely as possible, while air is circulated by the 15.24-cm. (6-inch) fan driven by a motor at approximately 400 r. p. m. The cabinet is constructed of a wood frame rabbeted to fit 6.35-mm. (0.25-inch) waterproofed Masonite board, the joints being sealed with several coats of shellac. The

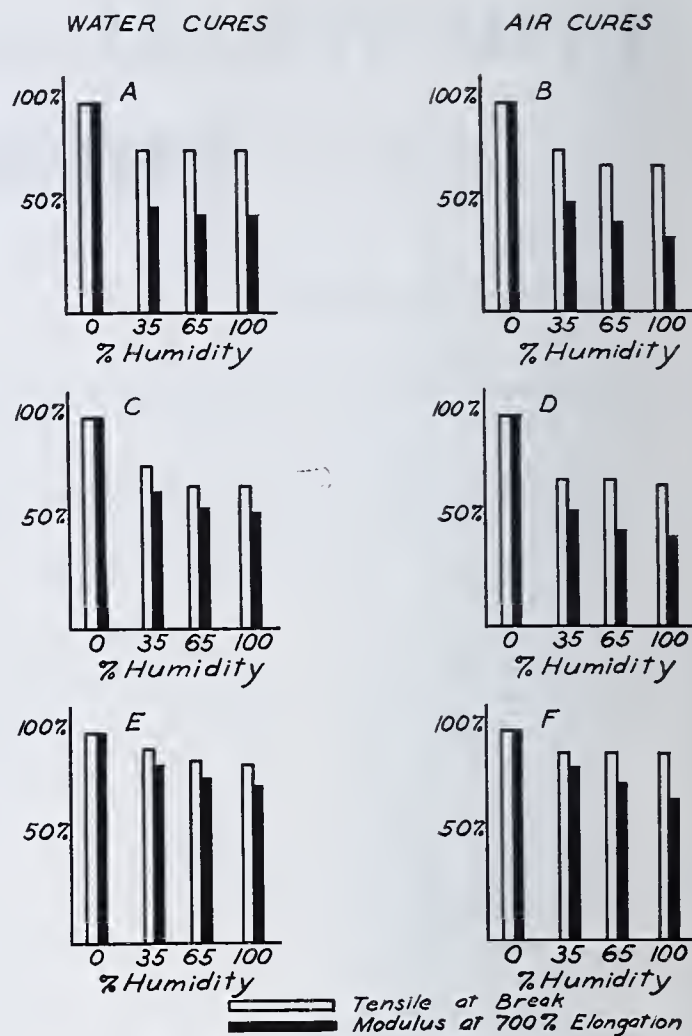


FIGURE 3. TEST RESULTS

door is fitted like a refrigerator door on soft-rubber-tubing gaskets.

In order to study the effect of humidity on latex test strips, eight films were dried as above. Four films were cured in water at 100° C. and four in air at 85° C., over the standard range of cures. Three test strips from each cure were suspended for 48 hours in desiccators containing various concentrations of sulfuric acid (5) so as to give humidities of 0, 35, 65, and 100 per cent, respectively (6), at 21.2° C. (70° F.) before testing. The test pieces were removed from the desiccator in quantities which could be broken on the test machine in less than 30 minutes, which exposure has shown no effect on physical tests and has shown a saving in time when compared with removing the test pieces individually. The physical test results on the conditioned test strips, as affected by the various humidities, are shown in Figure 3. These data were obtained by taking the average of the tensile results, and the average of the 700 per cent modulus results over the complete range of cures at each humidity. The values at 0 per cent humidity, being the highest (7), are taken as 100 per cent, and the values obtained for the higher humidities are expressed as a certain per cent of the 0 per cent humidity values. Similar results are obtained by taking the values at optimum cure or any time of cure, since the effect of humidity is similar throughout the entire range of cures.

In the water cures the values obtained for 35, 65, and 100 per cent humidity are equal but below the 0 per cent humidity value (Figure 3, A), while the air cures (Figure 3, B) show a decrease in properties in the order of ascending humidity. This result probably is due to the extraction of water adsorbing materials during the water cure.

The differences in the effect of humidity between the air and the water cures were checked by the following method



A sample of 60 per cent latex which had been purified by triple centrifuging (2) was compared with the regular 60 per cent latex. This purified latex was very slow in curing with Pip-Pip acceleration in the standard formula; so this test was carried out using the formula in Table III, keeping the quantity of dispersing agents added comparable to that given in Table I by decreasing the sulfur.

TABLE III. LATEX FORMULA

	Dry Basis	Wet Basis
Rubber as 60% centrifuged latex	100.0	166.6
Zinc oxide as a 50% dispersion	1.0	2.0
Sulfur as a 50% dispersion	0.75	1.5
Piperidine cyclopentamethylene dithiocarbamate (Pip-Pip)	0.5	0.5
Di(benzothiazyl thiol) dimethyl urea	0.5	1.0
Water to 54% total solid content	...	18.9

Eight test films were prepared from each compound following the procedure given above. Four of each were cured in water at 100° C. and in air at 82° C. over a range of cures approximating those carried out on the formula given in Table I. Test strips for the complete range of cures were conditioned as above and tested. The effect of humidity on the physical tests is shown in Figure 3, *C, D, E, F*. The regular 60 per cent latex shows the same general trend as the standard test formula in both water (Figure 3, *C*) and air cures (Figure 3, *D*). The purified 60 per cent latex shows much less effect of humidity on physical properties of the cured test strips and practically no difference between the water (Figure 3, *E*) and air cures (Figure 3, *F*). This is because the purification process has removed the greater portion of the water-solubles present in the latex. Latex purified by this centrifuging process is known to have a nitrogen content below 0.10 per cent and to be very much less hygroscopic.

### Conclusions

Films should be prepared in an atmosphere free from air currents at 60 to 75 per cent relative humidity and at a temperature of 21.2° to 29.2° C. (70° to 85° F.) during the first hours of the drying period.

These films should be suspended for complete drying for an additional 48 hours at 0 per cent humidity and 10° to 15.5° C. (50° to 60° F.) before curing.

The water-cured films should be dried 3 hours in the open room followed by about 20 hours at 0 per cent humidity and 10° to 15.5° C. (50° to 60° F.) before the preparation of test pieces.

The air cures are kept in a desiccator for about 24 hours at 0 per cent humidity and 10° to 15.5° C. (50° to 60° F.) before the preparation of test pieces.

The die for preparing test pieces must have perfect cutting edges.

Test pieces should be conditioned 48 hours at 0 per cent humidity and 21.1° C. (70° F.) before testing to obtain maximum tensile and modulus results.

The effect of humidity on physical test will be greater on normal latex, Revertex, and stabilized latex because of their increased water-soluble constituents which increase water adsorption. Good averages are obtained from three of four test strips broken, but for accurate work the average of the best four of six test strips should be taken.

### Acknowledgment

The author wishes to thank the Monsanto Chemical Company for permission to publish this information, and the various members of the staff for helpful suggestions in its preparation.

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## Purification of Graphite for Spectrochemical Analysis

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GRAPHITE of fairly high purity is obtainable commercially but its impurities are of such a nature that its use in spectrochemical work is somewhat limited. For practically all qualitative and many quantitative analyses, it is highly important that the impurities commonly present in this material be entirely eliminated or reduced to the merest traces. A purer but much more expensive grade is also obtainable, but this is less uniform with regard to its impurities than the product obtained by the method described here.

TABLE I. IMPURITIES IN GRAPHITE BEFORE AND AFTER SULFURIC ACID TREATMENT

Original Impurities	After Treatment	Original Impurities	After Treatment
Aluminum	None	Manganese	None
Barium	Unchanged	Silicon	Unchanged
Bismuth	Trace	Silver	None
Copper	None to faint trace	Sodium	Trace
Lead	None to faint trace	Titanium	None
Magnesium	Trace	Vanadium	None

Standen and Kovach (1) have described two methods of purification which they have found to be satisfactory. Both methods, however, appear to be somewhat more involved and more consuming than the procedure described in this paper.

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The authors have found sulfuric acid more effective in the washing than nitric acid, hydrochloric acid, or aqua regia. Attempts to remove silicon with hydrofluoric acid were unsuccessful.

### Procedure

Cut the graphite into the desired form for use as electrodes. Heat in a silica dish over an oxy-gas burner to redness. Cool and place in a flask fitted with a reflux condenser. Cover the electrodes with 1 to 1 sulfuric acid and boil on a hot plate for at least 24 hours. Wash by decantation with distilled water until the water is no longer acid to litmus, then boil 15 minutes in a fresh portion of water. Again wash by decantation and repeat the boiling. Continue the alternate washing and boiling until acid is no longer extracted. Usually four such operations will suffice. Transfer to the silica dish and heat to bright redness, allowing the flame to play directly on the electrodes. Cool and store in capped bottles until used.

Table I shows the effectiveness of the treatment.

### Literature Cited

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RECEIVED December 28, 1937.



# Analysis of Commercial Phenothiazine Used as an Insecticide

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IN THE search for synthetic organic compounds that might replace the arsenicals now commonly used as stomach poisons for the control of various insects of economic importance, a great number of organic compounds have been prepared and tested. One compound, phenothiazine, has been found especially toxic to newly hatched codling moth larvae under laboratory conditions. It has also given a high degree of control of this insect in field tests in the Northwest, but because of certain practical difficulties it is not yet in commercial use.

The method for the preparation of phenothiazine on a commercial basis consists in heating 1 mole of diphenylamine with 2 atoms of sulfur at about 180° C., using iodine as a catalyst. The reaction is practically quantitative, and for use as an insecticide no purification of the product is necessary.

However, a dark green compound, which is insoluble in anhydrous ethyl ether, is formed in varying quantities. When tested against certain species of insects, this compound has been found to be relatively nontoxic.<sup>1</sup> Its chemical nature has not been fully determined, but it appears to be isomeric with, or a polymer of, phenothiazine.

Calculated for C<sub>12</sub>H<sub>9</sub>NS: C, 72.36; H, 4.52  
Found: C, 71.41; H, 4.31

The insolubility of this green material in anhydrous ethyl ether is utilized in analyzing commercial phenothiazine. A

<sup>1</sup> These results will appear as a scientific note in the *Journal of Economic Entomology*.

weighed amount of the compound is placed in a tared Soxhlet thimble and extracted with ether in the usual manner. The residue, which consists of the green material, is then determined from the increase in weight of the dried thimble.

Little or no unchanged diphenylamine has been found in samples of commercial phenothiazine. Diphenylamine is precipitated almost quantitatively, however, from an anhydrous ethyl ether solution by means of dry hydrogen chloride. This precipitate can be filtered on a tared Gooch crucible, washed with anhydrous ethyl ether, dried, and weighed. By this procedure, 97.2 per cent recovery, as the hydrochloride, was obtained from an ether solution containing a known quantity of diphenylamine.

Six samples of phenothiazine that were used in various field tests the past season were submitted to the Division of Insecticide Investigations for analysis. All material was purchased from the same manufacturer. The results are as follows:

Sample No.	Insoluble in Ether <sup>a</sup> %	Sample No.	Insoluble in Ether <sup>a</sup> %
1	1.14	4	1.34
2	1.43	5	1.09
3	1.21	6	1.23

<sup>a</sup> The analyses were carried out by Miss Ruth Capen of the Division of Insecticide Investigations.

RECEIVED December 2, 1937.

## Determination of Iron with *o*-Phenanthroline

### A Spectrophotometric Study

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IT WAS shown by Walden, Hammett, and Chapman in 1931 that the complex ion formed with ferrous iron and *o*-phenanthroline has a high oxidation potential and may be used as an internal indicator in certain oxidimetric analytical procedures (7). Previously Blau had given an extensive description of the properties of *o*-phenanthroline, along with the method of preparation (1). Saywell and Cunningham reported recently that one can make a quantitative determination of iron in small concentrations in various fruit juices and other products by comparing the color of the *o*-phenanthroline complex with that of a series of standards (5). Hummel and Willard (1A) have applied the method to biological materials.

The purpose of the present paper is to present a critical study of various factors which may affect the formation of the colored complex, including a study of the effect of varying concentrations of fifty-five ions liable to be encountered in routine analysis.

#### Apparatus and Methods

In the determination of iron in fruit products, as carried out by Saywell and Cunningham (5), the color comparisons were made in graduated test tubes and in a colorimeter. The development of the photoelectric spectrophotometer, described by Michaelson and Liebhaufsky (4), has provided a means of detecting very small color changes with a much higher degree of pre-

cision and accuracy than is possible with visual methods. General Electric recording instrument was used in all transmittancy measurements in this work. The cells were 1.00 cm. thick, the "blank" in the reference beam of light being filled with a solution containing the same amount of hydroxylamine hydrochloride and *o*-phenanthroline as was used with the iron in the other cell.

All pH measurements were made with a "universal" potentiometer and glass electrode, as described by Mellon (2).

The standard solution of iron was prepared by dissolving electrolytic iron wire in dilute hydrochloric, nitric, or perchloric acid. The solutions were then diluted to volumes such that 1.00 ml. contained 0.100 mg. of iron. A 0.10 per cent solution of *o*-phenanthroline was prepared by dissolving the monohydrate in doubly distilled, iron-free water. Saywell and Cunningham use an ethanol solution but the authors found that the reagent dissolved readily in water heated to about 80° C. It is important that the *o*-phenanthroline monohydrate be free from impurities. Certain contamination, at least, is evidenced by a pink coloration of the crystalline material, and a lowering of the melting point stated by Smith (6) to be 99° to 100° C. A 10 per cent solution of hydroxylamine hydrochloride, used as a reducing agent for the iron, was prepared by dissolving the c. p. reagent in doubly distilled water. Solutions used in the determination of interfering cations were prepared from the chloride or nitrate salts of the metals; the anion solutions were prepared from the sodium or potassium salts.

In making up all colorimetric solutions used in this study the following procedure was adopted: The required amount of the standard iron solution was measured out; 1.0 ml. of the



hydroxylamine hydrochloride was added to reduce the ferric iron; the solution was diluted to approximately 75 ml.; an excess of *o*-phenanthroline solution was added, 5.0 ml. being used with iron concentrations up to 4.0 p. p. m. and 10.0 ml. with higher concentrations; and the resulting solution was diluted to 100 ml. The pH value was then determined and any desired adjustment in acidity was made. The volumes of acid or base required for this adjustment never amounted to more than 0.1 ml. of 6 *N* hydrochloric acid or 6 *N* ammonium hydroxide, thus keeping possible error from dilution sources below 0.1 per cent. Solutions of possible interfering ions were added before the *o*-phenanthroline color was developed.

Calculations of apparent error due to interference by ions were made from transmittancy measurements by means of Beer's law,  $T_1 = T_2 \frac{C_1}{C_2}$ , where  $C_2$  is the concentration of iron in the standard solution and  $C_1$  is the calculated concentration after the possible interfering ion has been added. These calculations were made by means of a special color slide rule.

The error was calculated thus:  $\frac{C_2 - C_1}{C_2} \times 100 = \text{per cent "apparent error."}$  An apparent error of 2 per cent was arbitrarily set as the limit of negligible interference in the case of the added ions. Since visual methods of color comparison often have a precision not less than 5 per cent, it was necessary to set a lower figure in order to provide for other possible factors.

### The Color Reaction

The colored complex ion formed between the *o*-phenanthroline and the ferrous ion has been postulated by Blau (1) to be composed of three molecules of *o*-phenanthroline and one ferrous ion. The intensity of the color produced is determined by the amount of iron when there is an excess of the *o*-phenanthroline reagent present. It is this direct relationship between the iron and the intensity of the color which permits the use of the method.

The transmittancy curves for varying amounts of iron are shown in Figure 1. The peak of the absorption band is located at 508 m $\mu$ , with a secondary band shown at 474 m $\mu$ . Six parts per million of iron was found to be the maximum concentration which could be used with a 1.00-cm. cell. A concentration of 0.10 p. p. m. gave a minimum transmittancy of 95.5 per cent at this thickness. It would be possible to use less or more highly concentrated solution in a color comparator where very thick or very thin layers of solution might be used for comparative purposes.

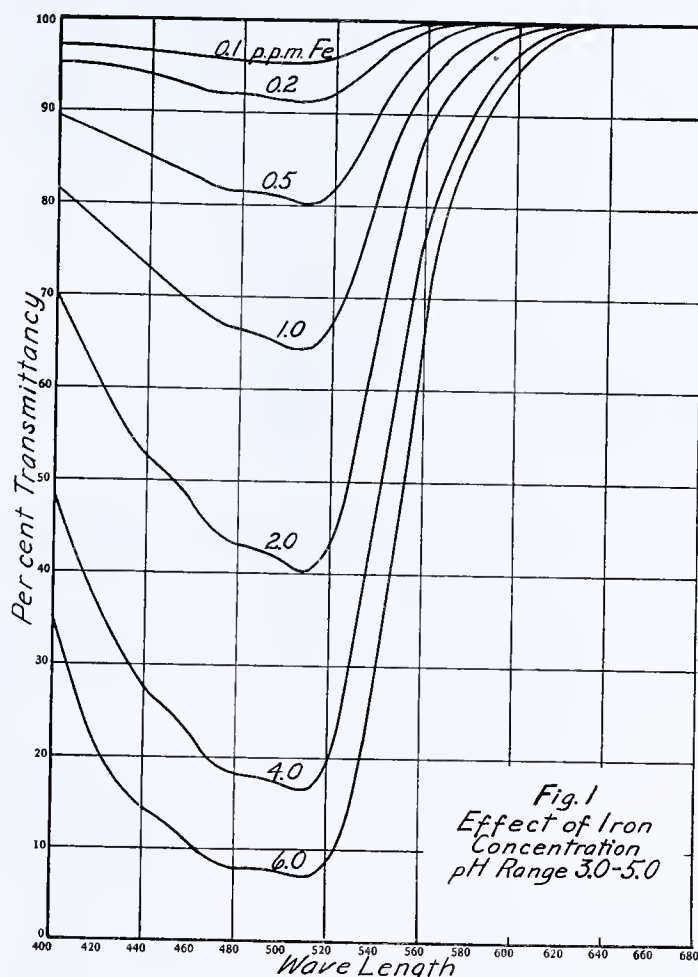
A study of the minimum amount of a 0.10 per cent solution of *o*-phenanthroline required to produce the maximum color revealed that 6.0 ml. of the reagent were required for every p. p. m. of iron present. Any amount less than this did not produce complete development of the color. This study was made by keeping the amount of iron constant and varying the total amount of *o*-phenanthroline added.

Transmittancy curves for solutions wherein the color was fully developed and the pH varied from 2.0 to 9.0 were exactly superimposed upon one another, showing that over this pH range the color was not dependent on the pH of the solution.

The conformity of the colored solution to Beer's law was tested over the range from 0.10 to 6.00 p. p. m. of iron, the units found applicable for a 1.00-cm. cell, by plotting  $2 + \log T$  against concentration. A straight line indicated very close conformity. Further tests were carried out by determining transmittancy curves on solutions in 1.00-cm. cells, diluting the solutions to exactly twice the original volume and again determining the transmittancy in 2.00-cm. cells. The two curves were superimposed on each other.

Accelerated, as well as ordinary, fading tests agreed well with Saywell and Cunningham's conclusions that the color is stable for at least 15 days. On one test, the solutions were

sealed in test tubes and exposed to varying degrees of light over a period of 11 days. The transmittancy curves on the original solutions and the same solutions after exposure were identical. In making the accelerated fading tests, the solutions were placed in glass-stoppered Pyrex bottles of about 60-ml. capacity after the transmittancy curves were determined.



These bottles were then placed in an air thermostat at 30° C. at a distance of 60 cm. from a mercury arc lamp for a period of 100 hours. Redetermination of the transmittancy curves indicated no fading. These solutions were then set aside for 150 days, when the transmittancy curves again agreed well within experimental error.

### Reducing Agents

Following the original work of Saywell and Cunningham, the authors used a 10 per cent solution of hydroxylamine hydrochloride as the reducing agent in all work on interfering ions and in concentration tests. Because of the relatively high cost of the reductant, it was decided to try certain other agents. A 10 per cent aqueous solution of sodium sulfite was tried with very unsatisfactory results. In slightly acid solution a brown colored complex was formed. The presence of the brown coloration proved to be a serious interference when the *o*-phenanthroline color was developed, causing errors varying from 4.5 to 37.5 per cent.

Sodium and potassium formates (analytical reagent) were found to be free from iron in appreciable quantities. However, determinations using these materials as reducing agents showed appreciable error. According to Mellor (3), this is probably due to the formation of a complex between the ferric ion and the formic acid formed in the solution.

Formaldehyde was used, but again a complex was formed between the iron and the reagent, causing appreciable error.

The hydroxylamine hydrochloride solution was found to be the most satisfactory for the reduction of the iron. The



relatively small amounts used and the speed with which the iron was reduced are sufficient to warrant the use of this reagent.

### Effect of Ions on Color Developed

Studies on the possible interference of ions were made in all cases on a solution containing 2.00 p. p. m. of iron. The iron was reduced with 1.0 ml. of a 10 per cent solution of hydroxylamine hydrochloride, the ion in question was introduced, the *o*-phenanthroline was added, and the solution was diluted to the mark. After mixing, the pH was adjusted with ammonium hydroxide or hydrochloric acid to a point within the range of applicable pH values shown in Tables I and II, and the transmittancy curves were determined. These curves were then compared with the standard for the same amount of iron without the added ions, and the per cent "apparent error" was determined as stated above.

It was decided that, with 2.00 p. p. m. of iron present, 500 p. p. m. of ion (250 times the concentration of iron in the solution) should be sufficient to test for interference. If this amount does not interfere, it is very improbable that the ion will interfere in any quantity.

**EFFECT OF CATIONS.** Of the large number of transmittancy curves obtained for cations, only certain representative ones are shown in Figure 2. They illustrate typical types of interference.

Table I gives the maximum concentration of ions and the applicable pH ranges which may be used without error in the determination of 2.00 p. p. m. of iron.

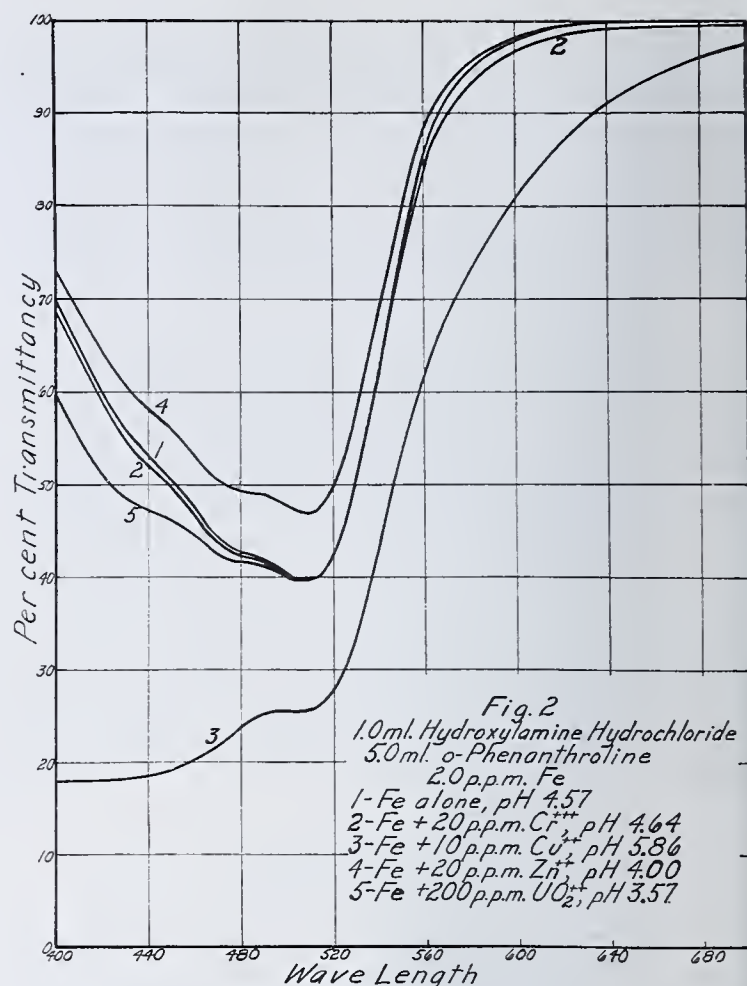
TABLE I. EFFECT OF CATIONS

Ion	Added as	Maximum Concentration, p. p. m.	Maximum Interference, % Fe	Applicable pH Range
Aluminum	AlCl <sub>3</sub>	500.0	None	2.0-3.0
		250.0	1.4	2.0-5.0
Ammonium	NH <sub>4</sub> Cl	500.0	None	2.0-9.0
Antimony	SbCl <sub>3</sub>	30.0	None	3.0-9.0
Arsenic	As <sub>2</sub> O <sub>3</sub>	500.0	None	3.0-9.0
Arsenic	As <sub>2</sub> O <sub>3</sub>	500.0	None	3.0-9.0
Barium	BaCl <sub>2</sub>	500.0	None	3.0-9.0
Beryllium	Be(NO <sub>3</sub> ) <sub>2</sub>	500.0	1.3	3.0-5.5
Bismuth	Bi(NO <sub>3</sub> ) <sub>3</sub>	None	1.0 <sup>a</sup>	3.0-9.0
Cadmium	Cd(NO <sub>3</sub> ) <sub>2</sub>	50.0	1.0 <sup>a</sup>	3.0-9.0
Calcium	Ca(NO <sub>3</sub> ) <sub>2</sub>	500.0	None	2.0-9.0
Chromium	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	20.0	None	2.0-9.0
Cobalt	Co(NO <sub>3</sub> ) <sub>2</sub>	10.0	1.5	3.0-5.0
Copper	Cu(NO <sub>3</sub> ) <sub>2</sub>	10.0	None	2.5-4.0
Lead	Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	500.0	None	2.0-9.0
Lithium	LiCl	500.0	None	2.0-9.0
Magnesium	Mg(NO <sub>3</sub> ) <sub>2</sub>	500.0	None	2.0-9.0
Manganese	MnSO <sub>4</sub>	500.0	None	2.0-9.0
Mercury	HgCl <sub>2</sub>	1.0	None	2.0-9.0
Mercury	Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	10.0	None	3.2-9.0
Molybdenum	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub>	100.0	None	5.5-9.0
Nickel	Ni(NO <sub>3</sub> ) <sub>2</sub>	2.0	None	2.5-9.0
Potassium	KCl	1000.0	None	2.0-9.0
Silver	AgNO <sub>3</sub>	None	...	...
Sodium	NaCl	1000.0	None	2.0-9.0
Strontium	Sr(NO <sub>3</sub> ) <sub>2</sub>	500.0	None	2.0-9.0
Thorium	Th(NO <sub>3</sub> ) <sub>4</sub>	250.0	1.5	2.0-9.0
Tin	H <sub>2</sub> SnCl <sub>6</sub>	20.0	None	3.0-6.0
		50.0	None	2.5
Tin	H <sub>2</sub> SnCl <sub>6</sub>	10.0	None	2.0-6.0
		20.0	None	2.0-3.0
Tungsten	Na <sub>2</sub> WO <sub>4</sub>	10.0	Negligible	2.5-9.0
Uranium	UO <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	100.0	None	2.0-6.0
Zinc	Zn(NO <sub>3</sub> ) <sub>2</sub>	10.0	None	2.0-9.0
Zirconium	Zr(NO <sub>3</sub> ) <sub>4</sub>	50.0	1.8	2.0-9.0
		100.0	2.2	3.0-9.0

<sup>a</sup> 15.0 ml. of *o*-phenanthroline in excess of the original amount added. Iron reduced with hydroxylamine hydrochloride in all tests.

Potassium and sodium showed no interference when present in quantities as high as 1000 p. p. m. The following cations may be present in concentrations as high as 500 p. p. m. over the applicable pH range without interference: ammonium, arsenic (as arsenate or arsenite), barium, calcium, lead, lithium, magnesium, manganese (as manganous ion), and strontium.

Chromic ion changed the hue of the solution by absorbing somewhat in the red and violet. There was no apparent



error in the minimum of the transmittancy curve with concentrations up to 50 p. p. m. However, at this concentration, the hue was quite different. At 20 p. p. m., there was very little change in hue and the solutions could be compared visually.

Bismuth and silver must be completely absent from the solution because of the formation of precipitates. In each case, the ion causing the precipitate came from the *o*-phenanthroline solution. At concentrations up to 30 p. p. m. of antimonous ion, no interference was noted. Concentrations above this precipitated insoluble basic salts. Beryllium showed no interference in concentrations up to 50 p. p. m. when the pH was kept between 3.0 and 5.5. Above pH 5.5 the hydroxide formed, and below 3.0 a complex was formed with the *o*-phenanthroline. Cadmium, mercuric, and zinc ions also formed precipitates with the *o*-phenanthroline. With small amounts of these ions it was possible to prevent appreciable interference by adding excess *o*-phenanthroline. When 15 ml. excess of reagent were added to 50 p. p. m. of cadmium ion, the interference dropped to 1.0 per cent. Ten parts per million of zinc ion appeared to be the limiting concentration without appreciable error. One part per million was set as the maximum concentration of mercuric ion which could be present.

pH was a very important factor in the interference of molybdenum, present as molybdate ion. At a pH of 4.0, a milky solution resulted with as little as 10 p. p. m. of molybdenum. Thirty parts per million caused serious error at a pH of 4.5, but did not interfere at a pH of 5.0. At pH values above 5.5, 100 p. p. m. of molybdenum could be present without appreciable interference.

Nickel ion produced a change in the hue of the solution. Apparently a complex was formed with the ferrous ion, the nickel ion, and the *o*-phenanthroline solution. At all wave lengths below 540 mμ the transmittancy was higher than normal, in proportion to the amount of nickel present,



reaching a maximum difference from the normal at about 480 mμ. Two parts per million of nickel was found to be the maximum concentration which could be present without interference.

Tungsten, present as tungstate ion, formed a complex with the ferrous ion present and caused a fading effect, evidenced by an increase in transmittancy. Ten parts per million of tungsten caused an apparent change in hue of the solution, evidenced by a decrease in the transmittancy in the longer wave lengths. At a concentration of 5 p. p. m. no interference was noted.

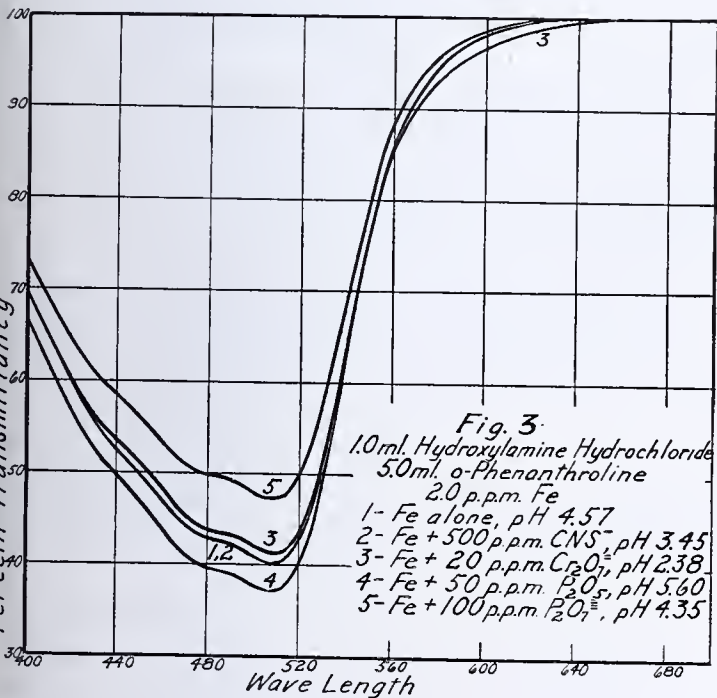
Certain other ions were rather limited in the pH range over which they might be present without interference. These conditions are indicated in Table I.

EFFECT OF ANIONS. Representative curves illustrating typical types of anion interference are shown in Figure 3.

Table II gives a summary of the limiting concentrations and the applicable pH ranges of the common anions encountered in routine analysis.

No interference was shown in concentrations as high as 500 p. p. m. for the following anions over the applicable pH range: acetate, bromide, chlorate, chloride, citrate, iodide, nitrate, sulfate, sulfite, and thiocyanate.

pH was a very important factor in the study of the anion interferences. Oxalate and tartrate showed no interference in concentrations as high as 500 p. p. m., provided that the pH was kept above 6.0 for the oxalate and above 3.0 for the tartrate.



Cyanide ion interfered most seriously of the anions studied. Apparently it formed a complex with the ferrous ion, from which the o-phenanthroline was not strong enough to remove all of the iron. Transmittancy curves on solutions containing this ion always showed a fading effect. Ten parts per million of cyanide ion could be present with 2 p. p. m. of iron with a maximum interference over the applicable pH range of just per cent.

Twenty parts per million of dichromate ion did not interfere with the quantitative color. However, amounts higher than this gave a change in hue which would prevent comparing these solutions with standards.

Nitrite ion did not interfere when the pH of the solution as kept above 2.5. At lower values nitrous acid was apparently formed and a brown coloration resulted.

Pyrophosphate ion in concentrations of 50 p. p. m. inter-

fered to the extent of 1.0 per cent when the pH was kept at 6.0 or above. Even as little as 20 p. p. m. interfered when the pH dropped to 5.5.

Thiosulfate ion was rather unique in that any interference it showed was due to the precipitation of free sulfur. The amount of sulfur precipitated was directly dependent upon the time that the solution was allowed to stand before measuring the transmittancy. Five hundred parts per million of thiosulfate ion showed no interference, provided the transmittancy curves were determined within 5 to 10 minutes after the solution was prepared and the color developed.

TABLE II. EFFECT OF ANIONS

Ion	Added as	Maximum Concentration, p. p. m.	Maximum Interference, % Fe	Applicable pH Range
Acetate	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	500.0	None	2.0-9.0
Tetaborate (as B <sub>2</sub> O <sub>3</sub> )	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	500.0	None	3.0-9.0
Bromide	NaBr	500.0	None	2.0-9.0
Carbonate	Na <sub>2</sub> CO <sub>3</sub>	500.0	None	3.0-9.0
Chlorate	KClO <sub>3</sub>	500.0	None	2.5-9.0
Chloride	NaCl	1000.0	None	2.0-9.0
Citrate	C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	500.0	None	2.0-9.0
Cyanide	KCN	10.0	2.0	2.0-9.0
Dichromate	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	100.0	Change hue	2.5-9.0
Fluoride	NaF	500.0	1.6	4.0-9.0
Iodide	KI	500.0	None	2.0-9.0
Nitrate	KNO <sub>3</sub>	500.0	None	2.0-9.0
Nitrite	KNO <sub>2</sub>	500.0	None	2.5-9.0
Oxalate	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	500.0	None	6.0-9.0
Perchlorate	KClO <sub>4</sub>	100.0	1.2	2.0-9.0
Phosphate (as P <sub>2</sub> O <sub>5</sub> )	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	20.0	1.4	2.0-9.0
Pyrophosphate	Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	50.0	1.0	6.0-9.0
Silicate	Na <sub>2</sub> SiO <sub>3</sub>	20.0	1.0	5.5-9.0
Sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	100.0	None	2.0-5.0
Sulfite	Na <sub>2</sub> SO <sub>3</sub>	500.0	None	2.0-9.0
Tartrate	(NH <sub>4</sub> ) <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	500.0	None	2.0-9.0
Thiocyanate	KCNS	500.0	None	3.0-9.0
Thiosulfate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	500.0	None <sup>a</sup>	3.0-9.0

<sup>a</sup> Transmittancy determined within 10 minutes after color developed. Iron reduced with hydroxylamine hydrochloride in all tests.

The degree of interference of several of the other ions was directly influenced by the pH of the solution, as may be seen from Table II. In nearly every case, however, it is feasible to adjust the pH to a region where the interference is at a minimum.

Discussion

The interference of some of the ions studied was probably due to the formation of iron complexes from which the o-phenanthroline was unable to remove all of the iron. Certain other interferences were due to the formation of an insoluble compound of the iron with the o-phenanthroline. In a few cases the interference was due to the color of the added ion, changing the hue of the solution itself.

While the limiting concentration of the iron was set as 6.0 p. p. m. in a 1.00-cm. cell, through a process of dilution one could determine much larger quantities in an unknown sample.

One of the serious disadvantages often found in the colorimetric determination of iron—namely, color formation in an alkaline solution with a consequent precipitation of many of the metal hydroxides or hydrated oxides—was not present in this method, wherein pH had very little effect on the color itself and the solution could remain acidic throughout the determination. Any common indicator paper, such as nitrazine paper, could be used as a rough check on the pH of the solution before color comparison.

The great advantages of the method are its sensitivity and its freedom from interference by most of the common ions. The very low amounts of iron which can be quantitatively determined by this method permit its use not only for routine food and biological analyses, but also for determination of purity of inorganic reagents.



### Summary

A spectrophotometric study indicates that Saywell and Cunningham's method of using *o*-phenanthroline for the determination of iron is very satisfactory for small amounts. It is more sensitive than the more common methods, the range being from 0.10 to 6.0 p. p. m. in a 1.00-cm. comparison cell.

Hydroxylamine is the best reductant studied. One-tenth milliliter of an aqueous 10 per cent solution is required to reduce each p. p. m. of iron completely from the ferric to the ferrous state.

Sodium sulfite, sodium formate, and formaldehyde are unsatisfactory as reductants, owing to the formation of complexes with the ferric iron.

Six milliliters of an aqueous 0.10 per cent solution of *o*-phenanthroline are required to produce the maximum color with 5.0 p. p. m. of iron.

The color reaction conforms to Beer's law over the entire range of concentrations studied. Visual comparison is thus applicable.

pH has no effect on the intensity of the color over the applicable range, 2.0 to 9.0.

The color is stable and does not change over a period of

6 months, including 100 hours under ultraviolet radiation during an accelerated fading test.

There are very few ions that seriously interfere with the production of the quantitative color reaction. A study of fifty-five possible interfering ions was made.

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# Quantitative Spectrochemical Analysis

## Chemical and Metallurgical Applications

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QUANTITATIVE spectrochemical methods have been developed at The Dow Chemical Company to a position of regular use for control analyses of many commercial products, including, among others, magnesium metal and its Dowmetal alloys, plastics, and pharmaceuticals. The speed and sensitivity of the spectrographic method contribute markedly also to the more rapid conclusion of research on new products and to the production of better materials through closer control of the manufacturing processes.

The saving of time and expense and the particular fitness for the analysis of materials for elements present in extremely small concentrations constitute important advantages of the method. In general, the method saves a considerable portion of the time and cost required for a chemical analysis. Moreover, the accuracy of spectrographic analysis of materials for elements occurring in concentrations of only a few thousandths of a per cent is extremely valuable, for in many instances this method provides the only practicable means of analysis.

Suitable analytical spectral sources and technics are used for the analyses of different chemical and metallurgical materials to obtain maximum sensitivity, rapidity, and accuracy. The spectral sources used include condensed sparks, high-voltage alternating current (1) and direct current arcs, and the cathode layer of the direct current arc (6, 10). The quantitative analytical procedures are based upon the correct correlation of the concentration of an element in the specimen with the actual intensity of the radiation emitted by that element under controlled conditions of excitation in a luminous discharge (3). These methods use internal standard elements (4), intensity calibration of each plate by a

step-slit (5, 11), and graphical conversion of microphotometer readings into percentage concentrations.

Extremely pure graphite for use as spectroscopic electrode supports is obtained by the use of high-temperature heating in an evacuated furnace.

Several thousand quantitative determinations are ordinarily made each month in routine fashion upon chemical and metallurgical materials. The concentrations of the elements under analysis in these materials vary from 0.0001 per cent to several per cent.

### Quantitative Analysis in Production Control

The basis of the technic is the experimental determination of the relationship between the concentration of a constituent of a specimen and the relative intensity of selected lines of that constituent and of an internal standard element in the specimen. The internal standard element may be the major constituent of the specimen or may be an element added in constant concentration. The relative intensity is obtained by means of an intensity calibration pattern placed upon each plate with a step-slit according to one of the accepted methods (5, 11).

No one spectral source is best adapted to the analysis of all types of materials; hence the source used for the analysis of any specified material should be that one found by experiment to possess the optimum qualities for that analysis.

The blackenings (defined as the difference between the peak of the galvanometer deflection of the microphotometer for the spectral line and the deflection for the transparent photographic plate) of the steps of the intensity calibration pattern and of the spectral lines are obtained with a photo-



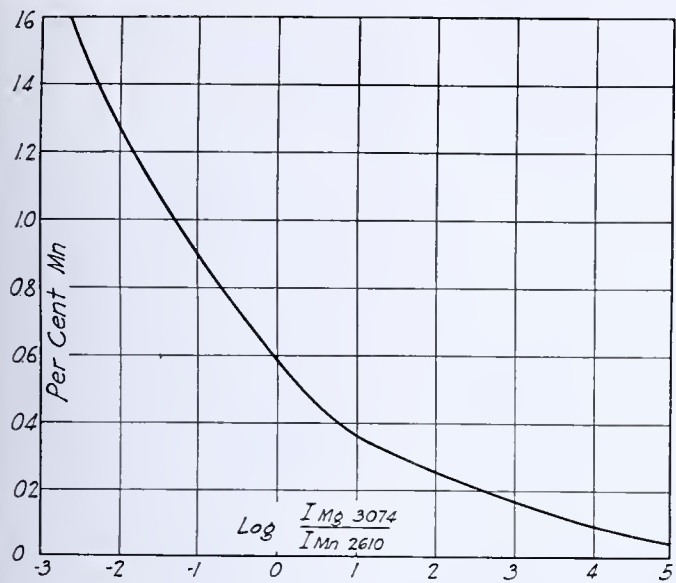


FIGURE 1. ANALYTICAL CURVE FOR ANALYSIS OF MAGNESIUM ALLOYS FOR MANGANESE

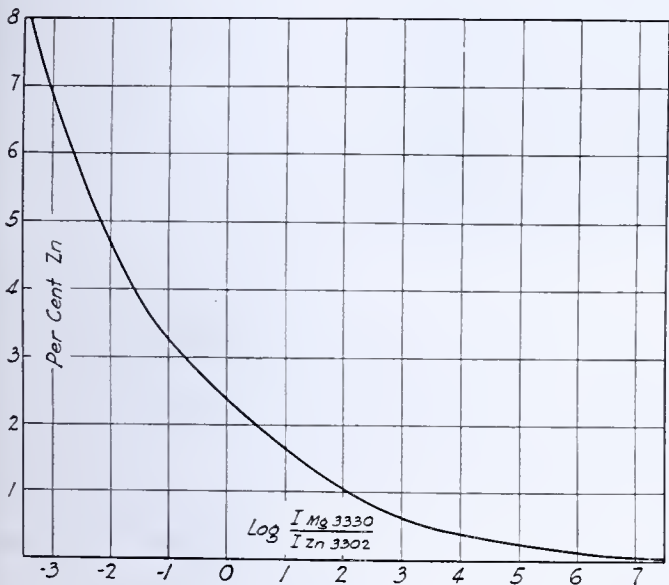


FIGURE 2. ANALYTICAL CURVE FOR ANALYSIS OF MAGNESIUM ALLOYS FOR ZINC

electric, nonrecording microphotometer. From the blackenings of the steps of this pattern a blackening-logarithm of intensity, characteristic curve for the plate is drawn. The relative intensity of the selected line pair is determined from this curve. This procedure, carried out for a series of specimens of known composition in which the concentration of the element under analysis varies over the desired range, yields an analytical curve for the analysis for this element (9).

Representative analytical curves for the analysis of magnesium alloys are shown in Figures 1, 2, and 3. The analytical curves made for each element under test serve as the sole basis for future analyses of similar specimens.

The speed of routine analysis is increased by reducing to a single, graphical step the conversion of spectral line blackenings, obtained with the microphotometer, into percentage concentration of the element under analysis.

Quantitative spectrochemical methods are used for production control analyses of several metallurgical and chemical plant products. Illustrations of these materials comprise magnesium metal and its alloys, plastics, and pharmaceuticals. In addition to the analyses now in regular use, the development of analyses of other plant products is being carried on.

MAGNESIUM METAL AND ALLOYS. Control analyses of magnesium metal and of its alloys are made chiefly by spectrochemical methods (8). These materials are analyzed for

some or all of the alloying constituents and impurities in the following usual concentration ranges:

	Per cent		Per cent
Manganese	0.001 to 3.0	Zinc	0.10 to 8.0
Silicon	0.001 to 1.5	Cadmium	1.0 to 6.0
Copper	0.01 to 0.10	Calcium	0.06 to 0.50
Aluminum	{ 0.01 to 0.10 2.0 to 13.0	Iron	0.001 to 0.045
		Nickel	0.001 to 0.05

Solid alloy electrodes are used. The analyses for manganese, silicon, copper, aluminum, zinc, cadmium, and calcium are made with a condensed spark spectral source. The analyses for iron and nickel are made with a direct current arc source, for which the electrodes are supported in water-cooled holders.

TABLE I. COMPARATIVE ANALYSES OF MAGNESIUM ALLOYS

Manganese		Zinc	
Spectrographic	Chemical	Spectrographic	Chemical
%	%	%	%
0.125	0.118	1.07	1.09
0.14	0.14	1.12	1.09
0.17	0.16	2.13	2.13
0.166	0.160	2.23	2.17
0.20	0.17	2.64	2.59
0.152	0.160	2.45	2.62
0.179	0.175	2.98	2.72
0.22	0.21	2.81	2.72
0.23	0.24	2.77	2.74
0.26	0.26	2.82	2.77
0.23	0.27	2.76	2.89
0.273	0.280	3.01	3.04
1.08	1.07	2.92	3.24
1.20	1.23	3.95	4.20
1.43	1.49	4.09	4.20

The majority of the specimens to be analyzed are received by this laboratory in groups of ten or more. An average of four determinations is made upon each specimen.

Under the present experimental conditions the time required for a duplicate determination is 5 man-minutes. This is roughly one-sixth of the time required for a chemical analysis.

In the usual concentration ranges of the elements under analysis, the accuracy of the routine spectrographic method is comparable with that of the routine chemical methods, except in the case of the analysis for high aluminum. In this instance the small change of aluminum spectral line intensity with concentration decreases the accuracy to some extent. However, the accuracy of the spectrochemical analyses for low copper and especially for nickel is considerably greater than that of the routine chemical methods.

Table I shows comparative analyses for manganese and zinc by spectrographic and chemical methods made in ordinary routine practice. These analyses were chosen at

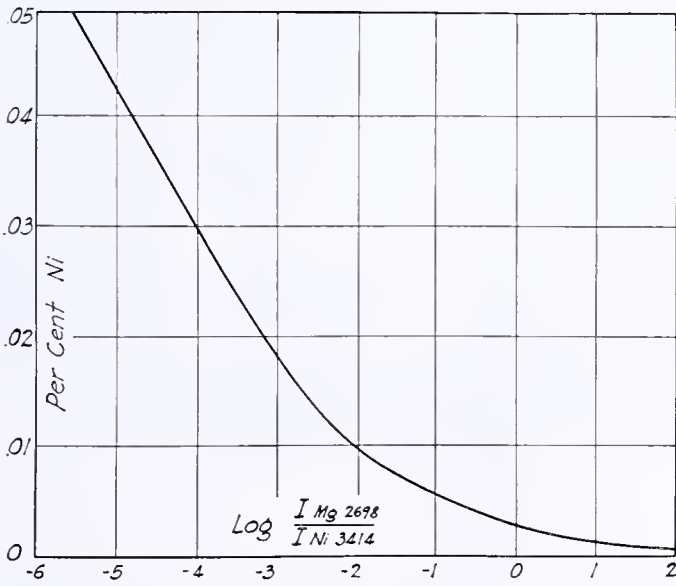


FIGURE 3. ANALYTICAL CURVE FOR ANALYSIS OF MAGNESIUM METAL AND ALLOYS FOR NICKEL



random from a list of about 100 for each, made over a period of 3 months.

With the exceptions of the analyses for elements present in concentrations of the order of 0.001 per cent and for high aluminum, the average error of the spectrochemical analysis amounts to approximately 5 per cent of the amount present.

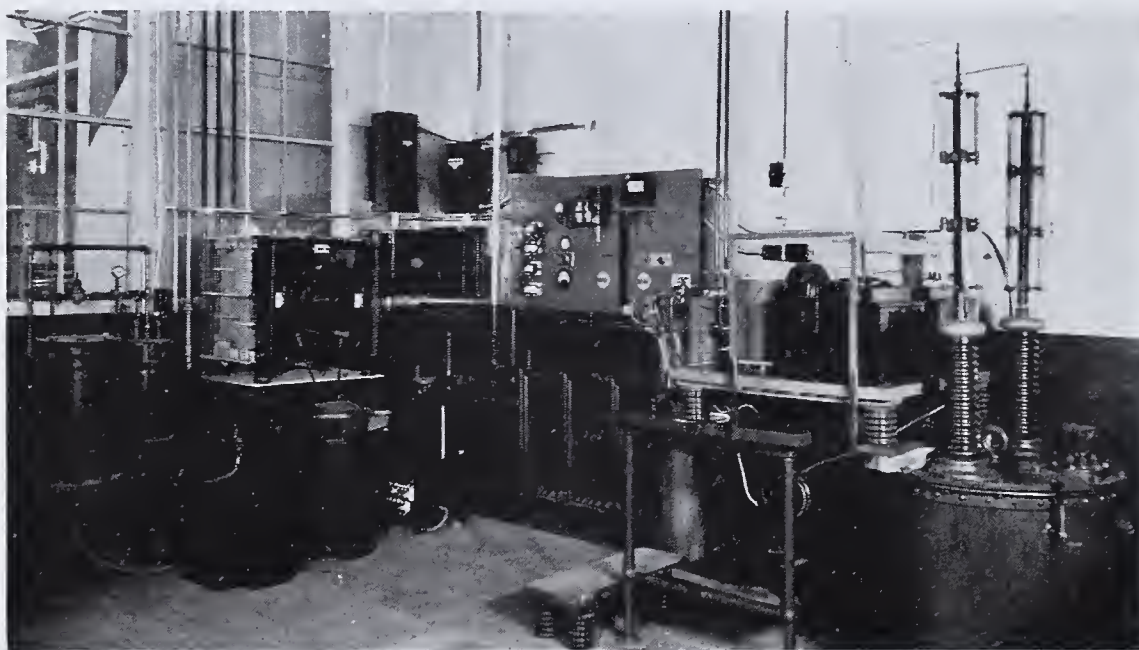


FIGURE 4. SPECTROSCOPIC SOURCE EQUIPMENT

For production of condensed sparks, direct current arc, and high-voltage alternating current arc

**PLASTICS.** The spectrographic method is well adapted for production control analyses of plastics for metallic impurities. By this method ethyl cellulose is analyzed for the following impurities in the concentration ranges given:

	Per cent		Per cent
Iron	0.001 to 0.02	Copper	0.001 to 0.03
Nickel	0.001 to 0.02	Sodium	0.005 to 0.50

The sample is prepared for analysis by digestion in concentrated nitric acid and an internal standard element is added to the resulting solution. A few drops of this solution are evaporated on graphite electrodes and the spectrum of the dry salt residue is produced by excitation in a direct current arc.

Under the usual conditions of analysis of a batch of six samples, the time required for one determination is about 17 man-minutes. The development of this analysis was carried out only to the point at which the accuracy required was obtained. This accuracy corresponds to possible errors of 10 per cent in the analysis for sodium and of 20 per cent in the analyses for the other metals. If required, these limits of error could be reduced by further refinement of technic.

Styrene and other plastics are analyzed for metallic impurities in a similar manner.

**PHARMACEUTICALS.** Control analyses for the production of sodium and potassium bromides provide an illustration of the use of spectrochemical methods in the manufacture of pharmaceuticals. The analyses of sodium bromide for potassium and of potassium bromide for sodium are carried out in the following concentration ranges.

	Per cent
Potassium	0.05 to 2.0
Sodium	0.01 to 2.0

Small portions of an aqueous solution of the bromide, made up to a definite concentration, are evaporated to dryness upon graphite rods which then serve as electrodes in

a direct current arc. The error in these analyses does not exceed 10 per cent of the amount present.

### Accessory Technic

The problems confronting an industrial spectrographic laboratory consist primarily of the development of analyses of greater sensitivity, rapidity, and accuracy, and of the practical use of these analyses on an economical, routine basis. The solutions of many of the problems which have confronted this laboratory have required the development of special equipment and technic.

**PURIFICATION OF GRAPHITE ELECTRODES.** Accurate analyses of many materials for small concentrations of metallic or metalloid impurities require the use of very pure graphite electrode supports. Commercial graphite of spectroscopic quality contains appreciable amounts of iron, silicon, boron, magnesium, calcium, copper, aluminum, titanium, and vanadium. The best grade of commercial graphite can be obtained only at considerable cost and even its purity is not completely

satisfactory. A simple, effective method of graphite purification has been developed in this laboratory which comprises heating at a temperature of about 2500° C. in an evacuated furnace (?). By this treatment graphite can be produced which contains practically no traces of any impurity, except boron, and is of higher purity than the best spectroscopic graphite previously commercially available.

**SPECTRAL SOURCE DEVELOPMENT.** In order to aid in the solutions of several analytical problems, considerable work has been carried out on the development and refinement of spectral sources most suitable for the analyses of different types of materials in which the constituents occur in concentrations varying from 0.0001 per cent to several per cent (?). Sources now in use consist of condensed sparks powered by

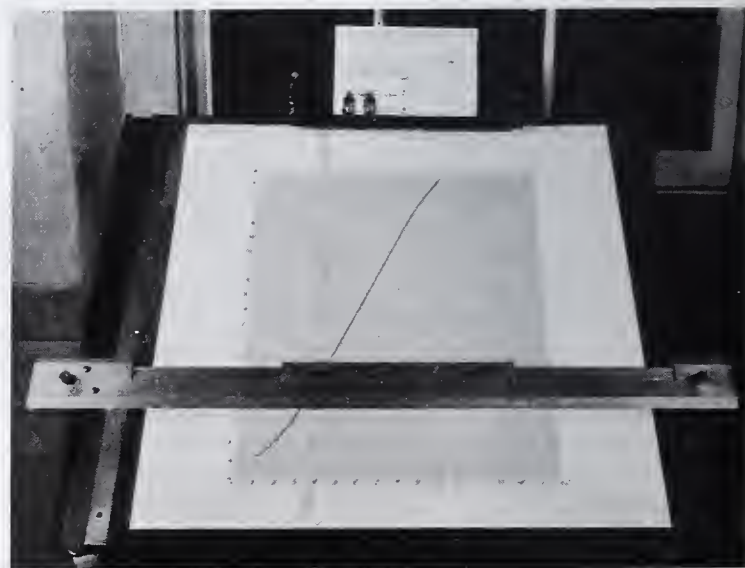


FIGURE 5. GRAPHICAL PLATE CALCULATOR

Coördinates of characteristic curve: ordinates, blackening; abscissas, logarithm of intensity



transformers yielding potentials up to 50,000 volts, the direct current arc, the cathode layer of the direct current arc, and the high-voltage alternating current arc. Figure 4 shows the equipment for these sources set up in a compact, switch-board-controlled form.

Condensed spark spectra have been found to yield greater accuracy than direct current arc spectra in the analyses of magnesium base alloys for the alloying constituents, but direct current arc spectra are required for the determinations of traces of some impurities. Similar results have been obtained by other investigators in the analysis of alloy cast iron (13).

The applicability of the high-voltage alternating current arc for analytical purposes was shown by Duffendack and Thomson (1). It has been found, both in the laboratory of Duffendack and his co-workers (2, 12) and in this one (7), that the sensitivity and accuracy of the high-voltage alternating current arc make this spectral source particularly well adapted to the analyses of many chemical materials. For the analyses of many industrial chemicals the sensitivity of the alternating current arc is comparable with or greater than that of the cathode layer of the direct current arc, while that of either is, in general, greater than that of the whole direct current arc. The advantages of the alternating current arc over the cathode layer for quantitative analysis consist of uniformity of spectral line intensity throughout the entire arc length ordinarily employed, much weaker background, and elimination of any optical system for accurately focusing a restricted portion of the arc upon the slit of the spectrograph.

**GRAPHICAL PLATE CALCULATOR.** In order to increase the speed of quantitative analysis in which an internal standard element is used, apparatus has been developed for graphical conversion of spectral line blackenings, obtained with a microphotometer, into percentage concentration of the element under analysis (7).

The calculator, illustrated in Figure 5, consists of a drawing board equipped with a straight edge constrained to move only in a direction perpendicular to its length. An analytical scale is prepared from the analytical curve for the analysis of the material for each element by projecting the ordinates in percentage concentration upon the abscissas in logarithm of relative intensity of the comparison spectral line pair. The preparation of an analytical scale for the analysis of magnesium alloys for zinc is shown in Figure 6.

The percentage concentration of each element under analysis is obtained by the procedure presented herewith.

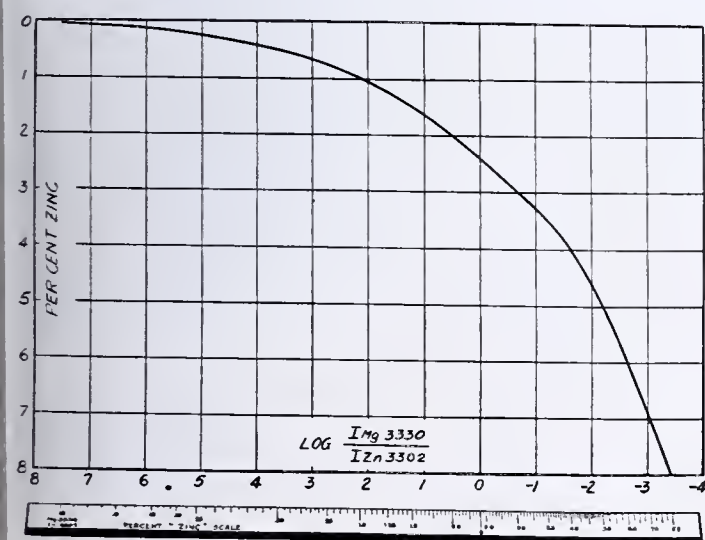


FIGURE 6. PREPARATION FOR GRAPHICAL PLATE CALCULATOR OF ANALYTICAL SCALE FOR ANALYSIS OF MAGNESIUM ALLOYS FOR ZINC

The appropriate analytical scale is placed upon the straight edge so that a fiducial mark on the scale intersects the characteristic curve of the plate, which is plotted on cross-section paper fastened to the drawing board, at the blackening of the selected line of the internal standard element. The straight edge is then moved until the scale intersects the characteristic curve at the blackening of the selected line of the element under analysis. The value read from the scale at this point of intersection is the percentage concentration of the latter element. The complete analysis of the specimen is made by repeating this procedure with the analytical scales prepared for the analyses for the different elements under test.

Use of this apparatus in routine control analyses has shown that it saves at least one-half the time required by arithmetical conversion of microphotometer readings into percentage concentrations, and that it reduces the probability of error.

## Summary

The quantitative spectrochemical method has proved its worth as an analytical tool in the metallurgical and chemical industries. Important advantages of the method include economy of time and material, and fitness for analysis of materials for elements present in extremely small concentrations.

As illustrations of the several thousand quantitative determinations made each month, the analyses of magnesium metal and its alloys, plastics, and pharmaceuticals are briefly described. The economy of the method is shown by the fact that the average time required for one determination, taking into account the analyses of all the chemical and metallurgical materials, is only 7 man-minutes. The corresponding time required by chemical methods is at least four times as great. The concentrations of the elements under analysis vary from 0.0001 per cent to several per cent.

The development of special equipment and technic, important for the attainment of greater sensitivity, accuracy, and rapidity of analyses in routine industrial use, is outlined.

## Acknowledgment

The writer wishes to express his appreciation to the staff of the X-Ray and Spectroscopy Department, particularly J. D. Hanawalt, Director, T. M. Hess, L. G. Reinhardt, R. G. Fowler, and J. S. Peake, for valuable suggestions and experimental assistance in this work.

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# Hydrolytic Precipitation of Cadmium Selenide from Selenosulfate Solutions

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CADMIUM selenide, despite its cost, has found application as a pigment in paints and ceramics. As a source of hydrogen selenide, it should also be of interest in the production of certain organic chemicals. In the paint industry, cadmium selenide is usually co-precipitated with barium sulfate by mixing solutions of cadmium sulfate and barium sulfide in which selenium has been dissolved (3). For use in ceramics, pure cadmium selenide may be made by a number of methods, most of which are not feasible commercially (2).

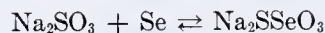
As an intermediate in certain organic syntheses, cadmium selenide offers many advantages, as pure hydrogen selenide is readily obtained upon acidification, and the soluble cadmium salt obtained in the generator is readily reconverted to selenide, thus effecting a material economy in the process herein described.

The proposed method (patent pending, assigned to the Chemical Foundation) for the preparation of cadmium selenide is based upon an experiment of Rathke (4), who found that upon addition of cadmium sulfate to potassium selenosulfate a white precipitate is formed, which changes through various shades of yellow and red to brown. By boiling this precipitate with dilute hydrochloric acid, he obtained cadmium selenide. Unfortunately, Rathke's article does not disclose his analytical methods. This reaction, rediscovered in the authors' laboratories, was found to be profoundly influenced by the temperature of precipitation, the acidity of the solutions, the rate of precipitation, and the amount of illumination.

TABLE I. REPRESENTATIVE RESULTS

(Pure CdSe = 41.26% Se)		
Temperature of Precipitation ° C.	Remarks	Se in Precipitate %
20	Agitated 17 hours	26.8
65	Agitated 8 hours	36.4
100	Boiled 1 hour. Stood 17 hours at room temperature	37.2

For this experiment, sodium selenosulfate was prepared by agitating amorphous selenium with a solution of sodium sulfite. An equilibrium is established,



the extent of the reaction depending upon the temperature. Apparently, the ion  $\text{SSeO}_3^{--}$  is formed, analogous to  $\text{S}_2\text{O}_3^{--}$ . The latter slowly decomposes, yielding  $\text{S}^{--}$ , by a reaction for which several mechanisms have been proposed (1, 5).

It is apparent that a number of reactions take place when solutions of cadmium sulfate and sodium selenosulfate are mixed. An over-all equation for the main reaction may be written:



## Experimental

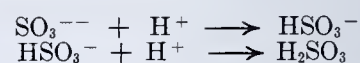
**EFFECT OF TEMPERATURE UPON PRECIPITATION.** When cadmium sulfate and sodium selenosulfate solutions are mixed in the stoichiometric ratio, precipitates of low purity and variable composition are obtained. Inasmuch as cadmium sulfite is only sparingly soluble, it precipitates along with the selenide, and the conversion of the former into the latter is very slow if the stoichiometric ratio of cadmium sulfate and sodium selenosulfate are used. Accordingly, the expedient

was adopted of using an excess of 25 per cent of the latter compound.

Table I gives representative results obtained at various temperatures. Only selenium was determined during the preliminary experiments, and the selenium content was used as a criterion of purity, because of the length of time required for a complete analysis.

**EFFECT OF ACIDITY UPON PRECIPITATION.** Accurate pH measurements with ordinary electrodes are not feasible in these solutions because of disturbing "redox" potentials and a tenaciously adherent film of cadmium selenide which separates out upon the surface of the reaction vessel and electrodes. Purely arbitrary limits of acidity and alkalinity were accordingly selected.

Assuming that acidification of sodium sulfite proceeds in two more or less distinct stages



it is evident that the limiting acidity compatible with an appreciable ( $\text{SO}_3^{--}$ ) [hence with an appreciable ( $\text{SSeO}_3^{--}$ )] is that of a solution of  $\text{HSO}_3^-$ .

Accordingly, a saturated solution of selenium in sodium bisulfite was prepared and treated with cadmium sulfate. No precipitate formed in the cold even after 2 hours, but upon heating the solution to boiling and allowing it to cool a precipitate formed, which, upon drying at 100° C., contained 30.6 per cent of selenium.

The limiting practicable alkalinity was considered to be that of an ammoniacal solution of cadmium sulfate containing just sufficient ammonium hydroxide to prevent the precipitation of cadmium hydroxide. After boiling a solution prepared in this manner, a precipitate containing 37.1 per cent was obtained.

Added acid or alkali in even very small amounts evidently produces an inferior product. Optimum results are obtained at that acidity at which the reactants sodium selenosulfate and cadmium sulfate come to equilibrium.

**EFFECT OF SPEED OF PRECIPITATION UPON COMPOSITION.** Since pure cadmium selenide could not be obtained even when  $\text{SSeO}_3^{--}$  was present in 25 per cent excess, the next phase of the problem was to determine whether a pure product could be precipitated by using such a small concentration of one reactant that precipitation would take place very slowly.

To use a large excess of cadmium sulfate and a trace of sodium selenosulfate plus sodium sulfite solution would be pointless, as enough  $\text{Cd}^{++}$  would be present to precipitate  $\text{SO}_3^{--}$  as well as  $\text{Se}^{--}$ . On the other hand, on adding a trace of cadmium sulfate to a substantial amount of sodium selenosulfate plus sodium sulfite solution, the product should be pure cadmium selenide as long as the solubility product of cadmium sulfite is not exceeded.

In an actual test, a cold dilute solution of cadmium sulfate was added to a cold solution of sodium selenosulfate plus sodium sulfite as long as the momentary white turbidity disappeared upon stirring. The solution was boiled gently for an hour, during which time a brownish crystalline precipitate formed of the composition

Cd	58.70%
Se	41.25%
	99.95%



The theoretical composition is

Cd	58.74%
Se	41.26%
	100.00%

This fractional precipitation may be repeated several times. In one experiment, three successive precipitations yielded precipitates, the average purity of which was 97.29 per cent.

**EFFECT OF LIGHT UPON THE COLOR OF THE PRECIPITATE.** Exposure to light darkens the color of the precipitate. Thus, solutions mixed in the dark in the stoichiometric ratio produced a white to canary-yellow precipitate of low but variable selenium content, whereas the precipitate formed by mixing the solutions in ordinary daylight was bright red in color. The light yellow tints were stable in the dark for hours, but a few seconds in direct sunlight sufficed to redden the exposed granules of the precipitate. Qualitative experiments with various filters indicated that radiation in the visible range was most effective. Quantitative studies, however, have not yet been made.

### Analytical

**SODIUM SELENOSULFATE SOLUTION.** The selenium content of the sodium selenosulfate solution was determined by adding a large excess of hydrochloric acid and weighing the precipitated selenium.

**SELENIUM DETERMINATION.** Digestion with aqua regia was unsatisfactory, as low, inconsistent results were obtained.

Excellent results were obtained by digesting the sample with a small quantity of sodium peroxide in about 5 cc. of water until all dark particles were converted into a white, gelatinous mass. (For a 0.1000-gram sample of cadmium selenide it is convenient to use 1 cc. of 30 per cent hydrogen peroxide and 0.5 gram of sodium hydroxide in a volume of about 5 cc.) A large excess of oxidant is to be avoided, because of evolution of chlorine in subsequent operations. An excess of hydrochloric acid was added, and sulfur dioxide was bubbled through the solution until the selenium precipitate was coagulated. (The solution should contain at least 90 per cent by volume of concentrated hydrochloric acid, in order to facilitate complete reduction of

hexavalent selenium by sulfur dioxide.) The selenium was weighed as usual.

**CADMIUM DETERMINATION.** A 0.1000-gram sample was dissolved in nitric acid in an Erlenmeyer flask equipped with a boiling valve to trap the spray. The excess acid was removed by evaporation, and the residue was fumed with 1 cc. of sulfuric acid. The resulting cadmium sulfate was then dissolved in about 5 cc. of water, and saturated sulfurous acid solution was added in successive small portions with intermittent warming, until selenium no longer precipitated. The solution was then filtered and heated gently to expel most of the sulfur dioxide. The last trace of sulfur dioxide was oxidized with potassium permanganate, which also served to oxidize any remaining traces of selenious acid to selenic acid. (The latter compound is less readily reduced at the cathode during the electrolysis which follows.)

A slight excess of oxalic acid was now added to reduce the excess potassium permanganate, and the solution was neutralized with sodium hydroxide, acidified with 1 cc. of acetic acid, diluted to nearly 100 cc., and electrolyzed between 50° and 70° C., using a platinum gauze cathode. (By beginning the electrolysis with the smallest voltage that will cause an appreciable current to flow, say 0.05 ampere, and after an hour increasing the current to 0.10 ampere, a smooth deposit, free from loose crystals, was obtained.)

After 3 or 4 hours a few cubic centimeters of water were added, and if no fresh deposit formed above the former solution level on the cathode, the electrolysis was interrupted, taking the utmost care lest the cadmium deposit be redissolved by the electrolyte after the cessation of the current. The cathode was thoroughly washed in distilled water, followed by alcohol and ether, and dried in an oven at 100° for 5 minutes or until the odor of ether was no longer perceptible. The gain in weight of the cathode was the weight of cadmium in the sample.

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## Determination of Ammonia and Urea in Milk

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**I**N CONNECTION with another investigation it was necessary for the writer to make determinations of ammonia in the milk produced by differently fed groups of cows. After unsuccessful experience with several of the methods found in the literature, an accurate yet simple method was devised which more nearly met the requirements.

A method has also been devised for the accurate determination of urea in milk, using chemicals and equipment found in most laboratories.

### Determination of Ammonia

The ammonia content of milk has been a matter of interest and study for at least 80 years, for Bouchardt and Quevenne in 1857 (2) are reported to have observed an ammonia content of 0.193 per cent in the case of milk made alkaline with sodium hydroxide before distillation. Of course this high result for ammonia was due to a breaking down of other nitrogenous compounds and did not represent a true value for ammonia or ammonium salts in the milk.

Modern history with respect to this determination may be said to begin with the work of Berg and Sherman (1) and of

Sherman and several collaborators (4, 15, 18). Milk itself was mixed with an equal volume of neutral methyl alcohol, using sodium carbonate as an alkali, and distilled under partial vacuum in a very large flask to overcome the pronounced tendency to foam. Values observed for fresh market milk from New York City and vicinity averaged around 0.39 mg. per 100 cc. Milk either untreated or preserved with formalin and stored 8 to 14 days showed values for ammonia up to 20 mg. per 100 cc.

Tillmans, Splittgerber, and Riffart (16) reported a series of results obtained by their own method of first precipitating the ammonia as ammonium magnesium phosphate from protein-free milk serum. After filtering and washing, this precipitate was distilled in the presence of alkali. Parallel determinations of ammonia by the Berg and Sherman (1) method showed remarkably good agreement.

Other groups of workers, notably Kieferle and Gloetzi (8), Burstein and Frum (3), and Kluge (9), have made different adaptations of the Folin and Bell (7) Permutit procedure originally designed for the determination of ammonia in urine. Recently, Niemczycki and Gerhardt (11), Polonovsky and Boulanger (14), and other groups of workers have reported the use of a combination of steam and vacuum distillation carried out on an aqueous deproteinized milk filtrate in an apparatus devised originally by Parnas and Heller (12), for the determination of ammonia in blood. This method would seem capable of accurate results, but the apparatus seems too complicated and limited in its application to make its general use at all probable.



**PREVIOUS METHODS.** The methods reviewed would seem to fall into two definite classes: (1) those using some form of distillation technic for separating ammonia from other milk components, and (2) those depending on some adaptation of the Folin and Bell (7) Permutit technic to accomplish this purpose. Values for ammonia in fresh milk obtained by methods of the first class fall in the range of 0.3 to 0.4 mg. per 100 cc. of milk, and the results are reasonably uniform (1, 4, 11, 14, 16, 18).

TABLE I. DEVELOPMENT OF AMMONIA IN MILK ON AGING

(Milligrams of ammonia nitrogen in 100 cc. of milk)						
	Fresh	24 Hours	4 Days	6 Days	8 Days	12 Days
Samples in Laboratory Window						
Raw	0.24	0.42	0.38	0.90	2.25	5.6
Pasteurized	0.35	0.42	0.43	0.48	0.48	5.0
	Fresh	48 Hours	7 Days	14 Days	21 Days	30 Days
Samples in Cooler at 5° C.						
Raw	0.28	0.30	0.42	1.55	5.63	11.0
Pasteurized	0.32	0.34	0.50	0.48	1.00	7.2

The results obtained by methods of the second class, using the Folin and Bell (7) Permutit adsorption principle, are decidedly different and more variable than those quoted above. Kieferle and Gloetzel (8) report ammonia values of 0.7 to 1.6 mg. per 100 cc. for the ammonia nitrogen content of fresh milk by this procedure. The writer in attempting to follow their method has demonstrated to his own satisfaction, however, that the high ammonia values reported by Kieferle and Gloetzel are due to a breaking down of urea during the heat precipitation of the lactalbumin in acetic acid solution.

This explanation seemed evident because samples of milk of high urea content were affected to a much greater extent than others of low urea content, and samples of pure urea subjected to the same treatment gave high values for ammonia. Burstein and Frum (3) and Kluge (9), using the Permutit adsorption principle, report ammonia values for fresh milk of around 0.1 to 0.2 mg. per 100 cc. or even lower in some cases. Burstein and Frum treat the milk itself directly with Permutit, while Kluge conducts the ammonia adsorption on the serum from trichloroacetic acid precipitation of the milk. Burstein and Frum do not mention recovery determinations, while Kluge claims satisfactory recoveries. The writer has repeatedly attempted to make determinations of ammonia in milk by the adsorption procedure, using both of the above and other modifications and has been unable to obtain what were considered to be satisfactory or consistent results. Recovery determinations of added ammonia were most unsatisfactory. The tentative conclusion was reached that the adsorption of ammonia on Permutit is unsatisfactory when applied to milk, probably because some material in the milk or milk serum inhibits satisfactory ammonia adsorption.

TABLE II. AMMONIA CONTENT OF PASTEURIZED MILK INOCULATED WITH PURE CULTURES OF VARIOUS BACTERIAL SPECIES

Name of Culture	Time Hours	Ammonia Nitrogen Mg./%	Time Hours	Ammonia Nitrogen Mg./%
Samples Held at Temperatures between 10° and 18° C.				
<i>Streptococcus lactis</i>	76	1.75	220	9.92
<i>Streptococcus liquefaciens</i>	76	1.15	220	4.05
<i>Aerobacter aerogenes</i>	76	1.50	220	4.30
<i>Bacillus subtilis</i>	76	0.90	220	1.35
<i>Escherichia coli</i>	76	0.87	220	1.25
<i>Lactobacillus bulgaricus</i>	76	1.08	220	1.25
<i>Pseudomonas fragi</i>	76	1.40	220	2.25
Bl. pasteurized milk	76	0.80	220	1.12
Samples Held at Laboratory Temperature, about 26° C.				
<i>Streptococcus lactis</i>	27	7.60	52	9.12
<i>Streptococcus liquefaciens</i>	27	1.30	52	1.72
<i>Aerobacter aerogenes</i>	27	3.30	52	5.37
<i>Bacillus subtilis</i>	28	0.90	52	1.15
<i>Escherichia coli</i>	28	0.35	54	0.60
<i>Lactobacillus bulgaricus</i>	28	1.08	54	2.00
<i>Pseudomonas fragi</i>	28	1.28	54	2.53
Bl. pasteurized milk	28	0.35	54	2.50

Some of the distillation methods quoted above depend on a low boiling point obtained by means of alcoholic solutions and distillation in partial vacuum to prevent the breaking down of the other nitrogenous substances to ammonia during the distillation of the latter. Other methods precipitate and remove these substances as far as possible before distilling. In the method described below the writer has sought to combine both these advantages.

**PROPOSED METHOD.** Kieferle and Gloetzel (8) made a comparison of various methods of milk protein precipitation. One of the most complete precipitants in the list studied was magnesium sulfate in combination with alcohol. However, Kieferle and Gloetzel made no use of this method, in connection with the determination of ammonia or urea. The filtrate from this precipitation has been used by the writer as a suitable medium in which to carry out both ammonia and urea determinations.

The alcoholic magnesium sulfate filtrate contains only about 30 mg. per 100 cc. of nitrogen based on the volume of the milk taken, whereas the milk itself contains from 400 to 600 or more mg. of nitrogen per 100 cc.; thus about 92 to 95 per cent of the nitrogen is removed from the scene of the reaction. The alcoholic filtrate boils about 20° C. below the boiling point of water, lessening the danger of decomposing the remaining 5 to 8 per cent of nonprotein nitrogen. Data presented in Table III show that the remaining nitrogenous constituents of this protein-free milk filtrate are little affected under the conditions of the distillation. Several samples have been distilled under a vacuum of 550 mm. The results in comparison with those obtained with the usual procedure were not appreciably affected by this added precaution.

TABLE III. EFFECT OF OTHER NONPROTEIN NITROGEN INGREDIENTS ON AMMONIA DETERMINATION

(Pure materials distilled as in the ammonia determination)		
Material	Amount Used Mg.	Ammonia Produced Mg.
Urea	5	0.035
Uric acid	10	0.10
Creatinine	10	None
Mixed amino acids	10	None
Glycine	10	0.01
Glutamic acid	10	0.01

The procedure found effective and convenient for ammonia determination in milk is as follows:

One hundred cubic centimeters of milk are treated with 20 grams of anhydrous magnesium sulfate. Alcohol of 85 to 95 per cent concentration is then added, with one intermediate shaking, to a final volume of 500 cc. The material is then filtered through a paper filter after standing a short time. The volume of filtrate which separates spontaneously may be increased to about 430 cc. by enclosing the paper filter in cloth and pressing by hand.

A 200-cc. portion of the above alcoholic filtrate representing 40 cc. of milk is transferred to a 500-cc. Kjeldahl flask and treated with 0.5 to 1 gram of magnesium oxide. Boiling is continued in the regular Kjeldahl nitrogen apparatus until 125 to 150 cc. of distillate are recovered, the ammonia being received in a solution of 0.00714 *N* sulfuric acid. The excess acid is then titrated with 0.00714 *N* ammonia, using a very dilute and carefully neutralized solution of methyl red as indicator. After deducting the proper blank value each cubic centimeter of 0.00714 *N* acid used represents 0.1 mg. of ammonia nitrogen.

**DISCUSSION.** The method calls only for standard equipment and chemicals available in most laboratories and is very economical of time. The blank due to reagents is very small and the recovery of added ammonia very good, as shown in Table IV. Increasing the alkalinity of the mixture at the time of precipitation by the addition of magnesium oxide or calcium hydroxide appeared to increase the recovery of added ammonia but it also increased the blank determination, as also shown in Table IV.



The amount of sample and reagents specified allows for distillation in duplicate. The amount of alcohol used may seem excessive, but most of this can be readily recovered by distillation from the acidified solution. The better grades of methyl alcohol or ethyl alcohol denatured with methyl would doubtless also be suitable where they are more readily available than ethyl alcohol. Some of the results obtained by the use of this method are shown in Tables I to V.

TABLE IV. DETERMINATION OF AMMONIA IN MILK

Recoveries	Recovery of Added Ammonia	
	2 mg. per 100 cc. added	10 mg. per 100 cc. added
	%	%
Milk + MgSO <sub>4</sub>	69-77	70
Milk + MgO + MgSO <sub>4</sub>	93-96	83
Milk + Ca(OH) <sub>2</sub> + MgSO <sub>4</sub>	89-100	90
Blanks		Ammonia
		Mg. %
MgSO <sub>4</sub> + alcohol		0.02
MgSO <sub>4</sub> + MgO + alcohol		0.10
MgSO <sub>4</sub> + Ca(OH) <sub>2</sub> + alcohol		0.17
Ammonia in MgSO <sub>4</sub>		0.002

Numerous claims have been made regarding the advantages of ammonia determination as a means of sanitary control (3, 9). Other than showing that ammonia development occurs chiefly as an accompaniment of prolonged bacterial action, no attempt is made in this article to confirm or deny such claims.

Many questions arise regarding the effect of different feeds, various production practices, differences in the condition of the cow, or different ways of processing or storing on the ammonia content of the milk. For most of these questions the available data are not sufficient to warrant very specific statements. Formerly it was believed that contamination with stable air and various impurities was largely responsible for ammonia in milk. Burstein and Frum (3) studied these factors but found no definite effect on the ammonia content of the milk.

Ordinary commercial pasteurization has little effect on the ammonia content of the fresh milk, but may have a marked effect on the subsequent course of ammonia development, as shown in Table I. It will also be observed from this table that ammonia developed very slowly. The increase was not at all marked until the sample showed other evidences of souring.

Table II shows the same slow development of ammonia for samples of pasteurized milk inoculated with pure cultures of various bacterial species when the samples were kept at relatively low temperatures. When samples of pasteurized milk were similarly inoculated but held at laboratory temperature, the ammonia production was greater in 27 hours than in 76 hours at the lower temperature (Table II). It is evident that the various bacterial species differ greatly in both rapidity and total capacity of ammonia production.

TABLE V. AMMONIA NITROGEN CONTENT OF MILK BY AUTHOR'S METHOD

	(Milligrams in 100 cc. of milk)		
	4 Cows, 21 Samples		Mean
	Highest	Lowest	
Low-protein feeding	0.60	0.27	0.42
	3 Cows, 20 Samples		Mean
	Highest	Lowest	
High-protein feeding	0.55	0.23	0.41

Other determinations of ammonia and of titratable acidity at regular intervals after inoculation seemed to show a possible relationship between these two values. The presentation of details regarding these points, however, is outside the scope of the present work.

In Table V is given the ammonia nitrogen content of milk from cows fed on low-protein rations in comparison with

that from others fed on high-protein rations. Apparently the intake level of protein does not affect the ammonia-nitrogen content of milk.

Determination of Urea

The presence in milk of considerable amounts of urea has been recognized by numerous workers during the past 20 years. Denis and Minot (5) suggested the treatment of milk directly with the Marshall (10) urease extract in determining its urea content, the milk so treated being later aspirated by the Van Slyke and Cullen (17) procedure for the removal of the ammonia formed. The ammonia was then determined, either by titration or nesslerization. The Denis and Minot method has been followed by other workers.

TABLE VI. TOTAL NITROGEN IN MILK PRODUCED ON DIFFERENT FEEDING LEVELS OF PROTEIN

	Low-Protein, Nutritive Ratio	Normal	High-Protein, Nutritive Ratio
	1:13		1:2
	%	%	%
Total nitrogen	100	100	100
Casein nitrogen	78.2	75.4	70.4
Albumin nitrogen, tannic acid precipitation	19.1	20.6	20.8
Residual or nonprotein nitrogen	2.7	4.3	8.8
Urea	0.7	1.9	4.5

In attempting to carry out urea determinations by this general procedure, the writer has found it preferable to use the filtrate remaining after the removal of casein or that remaining after the removal of both casein and albumin rather than the milk itself, because of the pronounced tendency of the milk proteins to break down with the formation of ammonia under the influence of even the mild alkalies used in the aeration. In the use of such deproteinized filtrates, however, care must usually be taken to avoid an excess of protein precipitant in the solution which is treated with urease, since many of the precipitants destroy or inhibit the action of this enzyme. The alcoholic magnesium sulfate filtrate described above, however, is favorable for the action of urease.

TABLE VII. UREA NITROGEN IN MILK

Cow	No. of De-terminations	Maximum	Minimum	Average
		Mg./100 cc.	Mg./100 cc.	Mg./100 cc.
Low-Protein Feeding				
293	3	8.0	5.2	6.2
301	10	7.2	1.7	3.5
362	9	9.2	1.6	3.6
Av. of 22 determinations				3.9
High-Protein Feeding				
329	3	27.4	20.8	24.3
332	9	22.4	17.5	20.3
414	5	28.7	20.7	25.0
Av. of 17 determinations				22.4

DETERMINATION. A convenient amount of the alcoholic magnesium filtrate described above (20 cc., equivalent to 4 cc. of milk) is used. One-half as much of a 5 per cent extract of Jack Bean meal in 25 per cent alcohol is added and the mixture is diluted to 200 cc., incubated for 2 hours at 40° C., or allowed to stand overnight at room temperature. One gram of magnesium oxide is then added and the distillation and titration of the resulting ammonia are carried out as directed above. After deducting the amount of preformed ammonia nitrogen from the observed value, the remainder may be considered as urea nitrogen or converted to urea by use of the factor 2.214.

Other principles of urea determination are available, but Van Slyke and Cullen (17) have shown that the urease decomposition is relatively complete and altogether a simple and reliable procedure. Complete aspiration of the ammonia by the Van Slyke and Cullen procedure requires approximately 2 hours, whereas the distillation of ammonia as described in the present paper can usually be carried out in 10 minutes. Commercial urease preparations may be used in place of the Jack Bean extract, if desired.



**DISCUSSION.** Data presented in Table VI, calculated from work previously published by the writer (13), show that urea nitrogen constitutes about one-half of the nonprotein nitrogen found in average milk. The proportion is larger in the case of milk from cows heavily fed on protein and is decidedly smaller in the milk from cows fed rations deficient in protein.

Denis and Minot (6) showed an apparent increase in the urea content of milk from the use of high-protein feeds. Data obtained by the writer and presented briefly in Table VII show that the urea content of milk is affected to a remarkable extent by the level of protein feeding. According to the author's observations (13) it is the only one of the nonprotein nitrogenous constituents of milk affected to any very marked extent by variations in the amount of protein fed.

### Acknowledgment

The author is indebted to H. H. Weiser, Ohio State University, for the pure cultures of bacteria described in Table II.

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# Determination of the Equivalent Acidity and Basicity of Fertilizers

## A Study of Mixed Indicators

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IN THE method for determining the equivalent acidity and basicity of fertilizers (9), the acid solution of the fertilizer is titrated by means of methyl red to an end point corresponding to the neutralization of the first hydrogen of phosphoric acid. That methyl red gives the desired end point was shown by the fact that the equivalent basicity values of mono-, di-, and tricalcium phosphates were found to agree with the theoretical values. With most solutions the end point of methyl red (first change in color from reddish pink to slightly orange pink) is easy to note, provided the titration is carried out under proper light conditions and a blank is used for comparison. Since most mixed fertilizers contain considerable amounts of phosphorus, however, the solution titrated is highly buffered and the color change per unit of base added is not as large as is ordinarily obtained in analytical procedures. The tendency among various workers, therefore, especially when inexperienced with the determination, is to titrate past the end point. Moreover, with solutions containing colloidal precipitates of iron and aluminum phosphate the appearance of turbidity may be mistaken for a change in color.

Horat (5) proposed the use of bromophenol blue instead of methyl red. Like all simple indicators, however, the transition interval of bromophenol blue extends over a range of about 1.0 pH unit, and it is difficult to describe the exact color change at the desired end point. Methyl red and bromophenol blue were compared by a number of collaborators of the Association of Official Agricultural Chemists, but there was no agreement as to which indicator was more satisfactory.

The ideal indicator for use in the determination of the equivalent acidity and basicity of fertilizers would give (1) the end point at the proper pH value, (2) a definite color change in both clear and turbid solutions, (3) a color change that can be easily described so that various workers will titrate to the same end point, and (4) warning of the approaching end point.

During recent years a greater amount of attention has been given to "achromatic" or other mixed indicators (6). Since

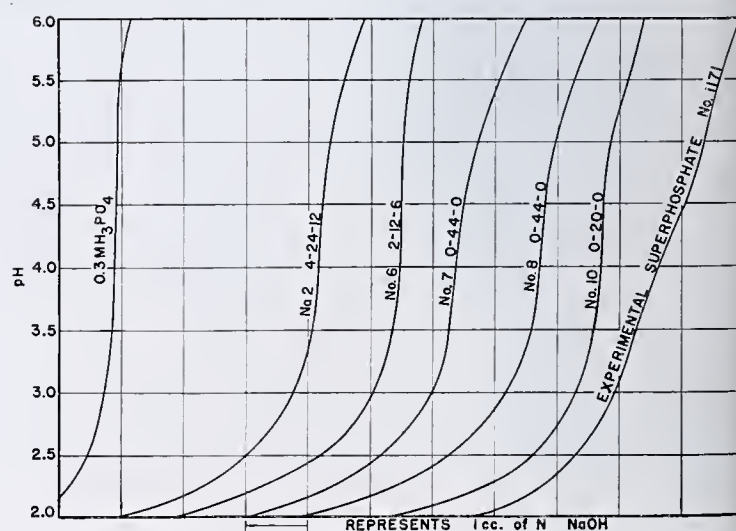


FIGURE 1. TITRATION CURVES OF PHOSPHORIC ACID AND OF ACID EXTRACTS OF VARIOUS FERTILIZERS



such indicators have a more definite transition point than do most simple indicators, it seems desirable to make a study of a number of mixed indicators to determine their merits as compared with methyl red and bromophenol blue.

Titration Curves of Phosphoric Acid and of Acid Extracts of Fertilizers

In order to get a better idea of the mixed indicators that might be suitable for this titration, a study was made of the titration curves of the extract of different mixed fertilizers. Britton (1) and others have shown that when phosphoric acid is titrated with a base, there is an abrupt break in the curve at the neutralization point of the first hydrogen. His data show, moreover, that the unbuffered or very slightly buffered portion of the curve extends from about pH 3.5 to 5.5. It is evident, therefore, that if the fertilizer solutions that are titrated in the determination of the equivalent acidity and basicity of fertilizers show as wide an unbuffered region, considerable leeway would be allowed in the choice of an indicator, for any indicator that gives a sharp change in color between pH 3.5 and 5.5 might be satisfactory.

TABLE I. DIFFERENCES IN EQUIVALENT ACIDITY AND BASICITY OF FERTILIZERS AS AFFECTED BY TITRATING TO DIFFERENT pH VALUES<sup>a</sup>  
(≈ lbs. CaCO<sub>3</sub> per ton)

Sample No.	Grade	pH						
		3.40	3.80	4.00	4.20	4.50	4.60	4.80
A-1	4-24-12	29B	14B	8B	5B	0	4A	13A
A-2	4-24-12	22B	13B	7B	4B	0	3A	11A
A-6	2-12-6	21B	10B	4B	1B	0	1A	2A
A-7	0-44-0	35B	21B	15B	11B	0	6A	34A
A-8	0-44-0	34B	20B	12B	6B	0	2A	32A
A-10	0-20-0	25B	12B	8B	3B	0	3A	8A
	Av.	27B	15B	9B	5B	0	3A	17A
Experimental super-phosphate No. 1171 <sup>b</sup>		79B	51B	37B	24B	0	6A	17A

<sup>a</sup> A refers to equivalent acidity, B to equivalent basicity (9).  
<sup>b</sup> Produced from a low-grade Tennessee brown phosphate rock high in iron, aluminum, and silicon.

Five representative commercial fertilizers were used for the study. These varied from 12 to 44 per cent in P<sub>2</sub>O<sub>5</sub> and were among those used by Horat (5) in his collaborative study. In addition, a superphosphate fertilizer prepared in the laboratory from a sample of rock phosphate very high in iron, aluminum, and silicon was included. The titration curves of these fertilizers (0.5-gram samples) and of a solution of 0.3 M phosphoric acid are shown in Figure 1. The phosphoric acid curve is similar to those of Britton in that it shows a very slightly buffered region between pH 3.5 and 5.5. The regular commercial fertilizers (curves II to VI, inclusive) also show a very slightly buffered region. As contrasted with the phosphoric acid curve, however, the slightly buffered region is much narrower, especially in curves IV and V. The least buffered portion of these curves extends from about pH 3.8 to 4.6, with the mid-point about 4.3.

The data presented in Table I summarize briefly the variations in the equivalent acidity and basicity of fertilizers that are obtained by titrating to different pH values. It is assumed for the purpose of this comparison that pH 4.5 represents the point at which the first hydrogen of phosphoric acid is neutralized. If the data for the six commercial fertilizers are first considered, it will be noted that only small differences were obtained when the end point is taken at pH values from 4.0 to 4.6. Even when the titration is carried to pH 3.8 the values obtained average only 15 pounds more basic (expressed as pounds of CaCO<sub>3</sub> per ton of fertilizer) than when the solutions are titrated to pH 4.5.

That certain fertilizers might be encountered which would show considerably greater buffer action within this pH range is indicated by the results obtained with the specially pre-

pared, experimental superphosphate. This fertilizer was prepared from a relatively low-grade Tennessee brown phosphate rock which contained 10.1 per cent of iron and aluminum oxides and about 6 per cent of silica. The results obtained with this superphosphate are shown in Figure 1 and also in the last line of Table I. The reason for the relatively high buffer action between pH 3.8 and 4.5 is not readily explained, since phosphoric acid solutions to which aluminum, iron, and calcium sulfate had been added did not show this buffered region. Fertilizers to which about 25 per cent of soil was added, however, showed about the same kind of curve as the experimental superphosphate. It is possible, therefore, that there is formation of calcium aluminosilicates or some complex of iron phosphate and dicalcium phosphate between pH 3.8 and 4.2 as indicated by the work of Kheifetz (7). It should be emphasized, however, that rock phosphate similar to the sample from which this superphosphate was prepared is not used commercially for the preparation of superphosphate fertilizers except in small amounts as fillers.

It seems apparent, therefore, from the data obtained with the commercial fertilizers studied (Figure 1 and Table I) that in the determination of the equivalent acidity and basicity of fertilizers the indicator used should show a well-defined change in color somewhere in the range of pH 4.0 to 4.6. Little practical significance need be attached in most cases to the small differences in the equivalent acidity of fertilizers obtained between these limits, although it would be desirable to obtain an indicator that would enable various investigators to titrate to within 0.2 to 0.3 pH unit. Since the mid-point of the slightly buffered portion of the curves is about pH 4.2 to 4.3, it would be preferable to obtain an indicator that would give the end point at about this range.

Comparison of Indicators

As previously mentioned, the color changes of the simple indicators occur over a rather wide pH range. In most cases there is a point of maximum color change within this range, but this point is not sufficiently distinct or easily recognized to make it possible to titrate to any definite pH value. In an effort to overcome these difficulties, various achromatic and other mixed indicators have been studied (3, 4, 5, 8, 10, 11), especially in recent years. A review of these studies has been given by Britton (1).

The principle of achromatic indicators is that by the addition of a dye which produces a color exactly the complement of the color of the indicator alone at its transition interval a gray or colorless solution will develop at a definite pH value. The constituent added may be a dye which does not change during the titration, or another indicator. On either the gray or colorless side of the point a color is produced, since the colors of the indicators or the indicator and dye are no longer complementary. The gray color appears only within a narrow pH range and it is thus possible to titrate to a definite pH value.

A brief summary of the results obtained with most of the indicators studied is given in Table II. Of these mixed indicators the indigo carmine-methyl orange is perhaps the most widely known. The color changes are distinct, violet (acid)-gray (pH 4.1)-green (basic), and the pH of maximum color change (pT value) is within the desired pH range. The indigo carmine decomposes upon standing, however, and the mixture deteriorates in only a few days.

A mixture of methyl orange and aniline blue of the concentration indicated in Table II was found to have a pT of about 4.3. The color changes from a violet to gray to a dull green, but the changes are rather gradual and the colors are not pure. The same criticism holds for acid blue or acid green with methyl orange. Methylene blue was found to give good color changes with either methyl orange or ethyl orange but the color changes were affected by the source of light.



TABLE II. PROPERTIES OF VARIOUS SIMPLE AND MIXED INDICATORS<sup>a</sup>

Indicator	pH Range or pT Value	Color Change	Remarks
Methyl red (0.2%)	3.8-6.0	Red-yellow	Color change gradual
Bromophenol blue (0.2%)	3.0-4.6	Yellow-blue	Color change gradual
Methyl orange (0.1%)	3.1-4.4	Red-yellow	Color change gradual
Bromocresol green (0.1%)	4.0-5.6	Yellow-blue	Color change gradual
Alizarin red S (0.1%)	3.7-5.2	Yellow-violet	Color change gradual
Methyl orange (0.1%)-indigo carmine (0.25%)	4.1	Violet-gray-green	Good color change; decomposes on standing
Methyl orange (0.1%)-aniline blue (0.1%)	4.3	Violet-gray-green	Colors not pure; change gradual
Methyl orange (0.05%)-acid blue (0.1%)	4.2	Violet-gray-green	Colors not pure; change gradual
Methyl orange (0.1%)-acid green (0.1%)	3.6	Violet-gray-green	pT too low; colors are not pure
Methyl orange (0.1%)-xylene cyanole (0.28%)	3.8	Violet-gray-green	Fair; green color weak; affected by light source
Ethyl orange (0.2%)-xylene cyanole FF (0.28%)	4.2	Violet-gray-green	Fair; green color weak; affected by light source
Methyl orange (0.2%)-methylene blue (0.05%)	3.9	Violet-gray-green	Fair; green color weak; affected by light source
Methyl red (0.13%)-methylene blue (0.083%)	5.2	Violet-gray-green	pT too high
Alizarin red S (0.5%)-methylene blue (0.063%)	4.3	Green-gray-wine	Good in clear solutions; precipitate absorbs dye
Methylene blue (0.03%)-bromophenol blue (0.1%)	3.5	Green-gray-blue	Fair change; pT too low
Methyl green (0.1%)-bromophenol blue (0.1%)	3.5-4.0	Green-blue	Shades too gradually
Methyl green (0.1%)-ethyl orange (0.2%)	4.3	Blue-gray-green	Color fades on green side
Bromocresol green (0.1%)-ethyl orange (0.02%)	4.5	Orange-yellow-green	Good color change in clear or turbid solutions
Bromocresol green (0.1%)-methyl orange (0.02%)	4.3	Orange-yellow-green	Good color change in clear or turbid solutions

<sup>a</sup> All concentrations are based on the use of 10 drops of indicator for 150 cc. of solution. The combinations listed using methyl orange were also tried using ethyl orange. The pT in all instances is somewhat higher, but the color changes are the same and the remarks are applicable.

The mixtures of xylene cyanole FF with methyl orange or ethyl orange were found to be somewhat more satisfactory than the methylene blue-methyl orange mixture, but they are subject to the same objections. The green color developed is weaker than is desirable, especially in turbid solutions, and the colors are affected by the source of light.

The various mixtures of methyl red with other indicators or dyes, such as methylene blue and bromocresol green, which have been referred to by Britton (1), were all found to show the maximum color change at too high pH values. The combination of methyl red with bromocresol green, however, is worthy of consideration for other types of titrations, for it gives in slightly buffered solutions a very abrupt change from red to green.

One of the most satisfactory indicators for clear solutions was a mixture of alizarin red S and methylene blue. The point of maximum color change is at about the desired pH value and the color changes from green to gray to wine are very distinct. Unfortunately, however, the mixture is not suitable for the titration of turbid solutions, for the precipitate absorbs the dye and the pT is lowered considerably.

The most suitable of the mixed indicators studied were combinations of bromocresol green with ethyl orange, methyl orange, or methyl yellow. All these combinations show very

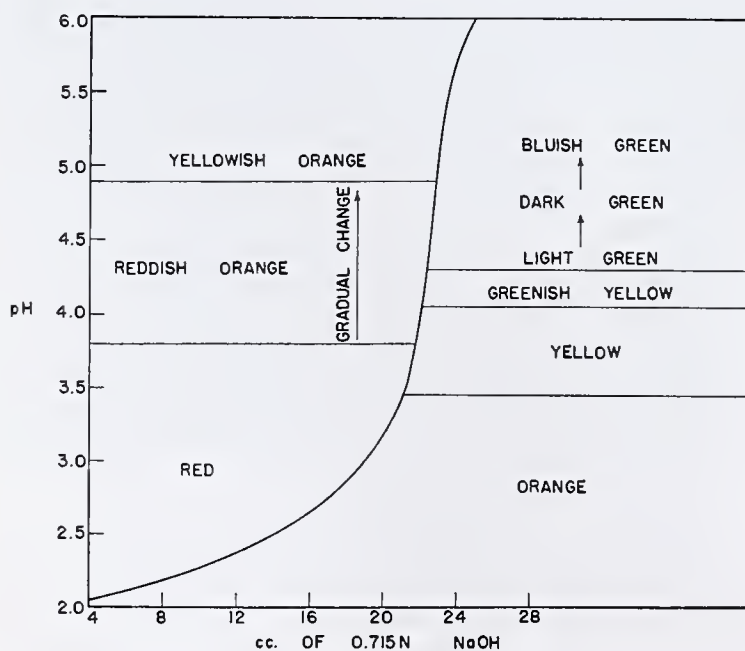


FIGURE 2. TITRATION CURVE OF  $\text{H}_3\text{PO}_4$  (0.03 M) AND  $\text{Al}_2(\text{SO}_4)_3$  (0.008 M)

Showing color changes of methyl red and of the methyl orange-bromocresol green mixed indicator

TABLE III. COMPARISON OF METHYL RED AND THE BROMOCRESOL GREEN-METHYL ORANGE MIXTURE IN DETERMINING EQUIVALENT ACIDITY AND BASICITY OF FERTILIZERS

Investigator	Fertilizer	Equivalent Acidity or Basicity <sup>a</sup>	
		Methyl red indicator	Bromocresol green-methyl orange indicator
W. R. Austin, Armour Fertilizer Works, Nashville, Tenn.	5-10-10	175 B	145 B
	0-10-4	634 B	638 B
	0-16-0	302 B	276 B
	0-20-0 experimental superphosphate No. 1171 <sup>b</sup>	30 A	78 A
H. B. Siems, Swift & Company Fertilizer Works, Chicago, Ill.	2-12-6	90 B	95 B
	Tailings	100 B	100 B
Authors	4-12-4	23 A	20 A
	5-8-7	498 B	471 B
	2-9-5	23 B	21 B

<sup>a</sup> Represents titration values only. A refers to equivalent acidity and B, equivalent basicity ( $\approx$  lbs.  $\text{CaCO}_3$  per ton).

<sup>b</sup> Made from low-grade rock phosphate high in iron, aluminum, and silica.

good color changes from orange to yellow to green, the main difference among them being in their pT values, the ethyl orange, as would be expected, giving the highest value and the methyl yellow the lowest. Of these the methyl orange-bromocresol green mixture is the most desirable for use in the method for determining the equivalent acidity and basicity of fertilizers, since its pT value is at about pH 4.3.

The color change of bromocresol green-methyl orange mixture is good in either clear or turbid solutions and the transition point is definite enough so that it cannot be mistaken. Figure 2 shows the color changes of the indicator as compared with those of methyl red. It will be noted that the orange color changes to a yellow at a pH of about 3.5, to a slight greenish yellow at about pH 4.05, and to a light green at about pH 4.30. This light-green color is taken as the end point, and may be described as the point where the green definitely predominates over the yellow. As would be expected, the solution becomes darker green as more alkali is added. The advantage of taking the light-green end point is not only that it comes at about the proper pH value but that it can be most easily described. Color changes at best are difficult to describe, and it is evident that in general the point of first definite appearance of a color or the first fading of the color can be more easily duplicated by different workers than intermediate intensities or shades of a color.

With methyl red the first change in color from red or reddish pink to orange pink or reddish orange takes place between pH 3.8 and 4.0. This is considerably lower than the lower pH limit of this indicator as given by Clark (2) and Smith (12) and no doubt explains why Horat and collaborators (5) ob-



tained values of greater equivalent acidity and also greater turbidity when using methyl red than bromophenol blue. It is apparent that they were titrating to a pH of near 5.0 or considerably past the first change in the methyl red color.

If the first change in methyl red is taken as the end point, it is evident from Figure 2 that the equivalent acidity or basicity values obtained with various fertilizers should not be much different from those obtained when the bromocresol green-methyl orange mixture is used, since the end points of both come in the very slightly buffered portion of the titration curve. That this is the case is shown in Table III. With those fertilizers that apparently give slightly buffered solutions, the difference between the two values is within experimental error; and where the differences are significant the equivalent basicity values, as would be expected, are slightly greater with methyl red than with the mixed indicator. The experimental superphosphate No. 1171 has been shown to be more highly buffered than most fertilizers between pH 3.8 and 4.5 (Figure 1 and Table I).



FIGURE 3. TITRATION APPARATUS

Bromophenol blue has a pH range or transition interval of 3.0 to 4.6 and the color change is from yellow to blue. The change, like that of methyl red, is rather gradual throughout the range and it is difficult to describe definitely any point within the range. Horat advocated taking the color change from yellow magenta to gray magenta. In the experience of the writers this point is found to occur somewhere near pH 3.5 to 3.8, although Horat considers this change to occur at pH 4.3 to 4.5.

**Preparation and Use of Bromocresol Green-Methyl Orange Indicator Mixture**

As with many other mixed indicators, the color change and the pT value are affected by the ratio of the two components of the mixture. This is shown in Table IV. The end point was found to be most definite when the indicator solution contained 0.02 per cent of methyl orange and 0.1 per cent of bromocresol green. With less of the former the yellow color was too weak, and with more the end point was not quite as definite. As the concentration of methyl orange is in-

TABLE IV. THE pT VALUE FOR BROMOCRESOL GREEN-METHYL ORANGE INDICATOR MIXTURE AS AFFECTED BY RATIO OF CONSTITUENTS<sup>a</sup>

Concentration of Constituents		pT Values Range <sup>b</sup>	Remarks
Methyl orange %	Bromocresol green %		
0.01	0.1	3.95-4.20	Too weak in methyl orange
0.02	0.1	4.25-4.35	Color change most definite
0.03	0.1	4.30-4.45	Disappearance of yellow not as sharp
0.05	0.1	4.45-4.75	Disappearance of yellow too gradual

<sup>a</sup> 10 drops of indicator (0.4 cc.) per 150 cc. of solution; and the change from yellow to light green (green definitely predominating over yellow) taken as the end point.

<sup>b</sup> The high values in each range represent those obtained with clear solutions; the low values, with very turbid solutions. The solutions used were highly buffered, being approximately 0.1 M H<sub>3</sub>PO<sub>4</sub>.

creased the color change occurs at a higher pH value. For these reasons it is important to prepare the mixture carefully, so that the proper amount of each indicator is used and both are brought completely into solution.

The most satisfactory method of bringing both indicators into solution is to weigh 0.1 gram of bromocresol green and 0.02 gram of methyl orange into an agate mortar, and to grind these with a pestle as small amounts of sodium hydroxide solution are added, using a total of 2 cc. of 0.25 N sodium hydroxide or its equivalent. The solution is transferred to a beaker and then to a 100-cc. volumetric flask and made up to volume with water.

Ten drops of the indicator mixture are used per 150 cc. of the solution titrated. While small variations from this amount give equally satisfactory results, it seems best to keep the ratio of indicator to solution to near one drop to 15 cc. of solution titrated.

The color changes described in this paper were obtained by using a simple home-made titration apparatus shown in Figure 3. This was prepared by fastening several white porcelain plates to the inside of a small box from which three sides had been removed and by attaching a light (using a blue daylight bulb) to a stand above and slightly back of the solution being titrated. This was found to furnish a much better source of light than is obtained with daylight. In fact, the use of such a lighting device is considered essential if consistent results are to be obtained in titrating slightly buffered solutions by means of indicators.

**Summary**

Since the two indicators that have been suggested in the determination of the equivalent acidity and basicity of fertilizers have not proved entirely satisfactory, further studies were undertaken, particularly with achromatic and other mixed indicators. Preliminary work showed that in most cases the buffer curve of the acid fertilizer solution titrated in the determination is only slightly buffered between pH of about 3.8 to 4.5. It was therefore concluded that one of the requirements of the indicator sought was that it should show a definite change in color at some point in this range, preferably at about pH 4.3 since this value represents about the mid-point of the slightly buffered portion of the curves.

A brief description of the shortcomings of a number of simple and mixed indicators is given. Several mixed indicators proved fairly satisfactory, but the mixture that was found most successful was a combination of bromocresol green and methyl orange. The qualities of the indicator that led to its choice are as follows: It shows a definite color change at the proper pH value and within narrow pH limits; the color change can be easily described; the end point is satisfactory in turbid as well as in clear solutions; and it gives warning of the approaching end point.

The advantages of this indicator over methyl red and bromophenol blue are discussed. Directions are given for



the preparation of the mixed indicator and attention is directed to the conditions under which the titration should be carried out, particularly regarding the use of artificial light (using a daylight bulb).

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## Confining Liquids for Gas Analysis

### Solubility of Common Gases in Acid Sodium Sulfate Solution

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IN A PREVIOUS paper (1) reporting the solubility of carbon dioxide in a number of salt solutions, it was concluded that an acidified solution of sodium sulfate was the most practical confining liquid for use in technical gas-analysis equipment.

The purpose of this investigation has been to determine the solubilities in this recommended solution of the gases and gas mixtures commonly encountered in technical gas analysis.

### Physical Properties

The solution of sodium sulfate used for this work was prepared by dissolving 200 grams of anhydrous sodium sulfate of analytical grade in 800 grams of distilled water and adding 40 ml. of concentrated (36 N) sulfuric acid of analytical grade. The solution was carefully boiled under a reflux condenser, cooled slightly, stoppered tightly, and cooled to 25° C. Solution for use was drawn from the bottom of the flask with a calibrated pipet.

**CRYSTALLIZATION TEMPERATURE.** The temperature at which crystal formation in the solution occurred was de-

termined, so that the lowest temperature for use without concentration change would be known. Sodium sulfate decahydrate was found to crystallize from the solution at 14.6° C. under conditions of violent shaking. Supersaturation appeared to be present at this temperature, as a considerable amount of soft mushy crystals precipitated. These crystals redissolved again between 16° and 18° C., but as equilibrium conditions were difficult to maintain while dissolving the crystals these temperatures tend to be high. The confining liquid cannot be used below about 16° C. without danger of precipitation.

**VAPOR PRESSURE.** The vapor pressure of the solution was determined by means of an isoteniscope modified to allow complete degassing of the solution without changing the concentration of the solution. The vapor pressure of the solution is shown as a function of temperature in Figure 1.

The data may be represented by means of the equation

$$\log P = 9.2675 - \frac{2375}{T}$$

### Solubilities of Single Gases

The apparatus used for the determination of the solubilities was that used previously (1). Two types of burets were used for this work. A mine-air buret was used for the more soluble gases, such as carbon dioxide, sulfur dioxide, acetylene, and nitrous oxide. This type of buret is accurate to 0.01 ml. in the range 75 to 100 ml. For the less soluble gases a 21-ml. Haldane buret was used. This has a calibrated range of 6 ml. accurate to 0.001 ml.; however, readings were taken only to the nearest 0.01 ml. A standard pressure compensator was used with the mine-air buret and an open-end manometer was used with the Haldane buret. Both burets were water-jacketed and maintained at 25° C. The technic was the same as previously employed. The partial pressure of the gas in the absorption bulb was maintained at 760 mm., as the vapor pressure of the solution was known. The time of shaking to reach equilibrium varied considerably between the two types of burets. With 100-ml. gas samples 20 to 30 minutes were sufficient, while with the 21-ml. samples 60 to 90 minutes were required because of the decreased liquid-gas contact area.

All the gases except carbon monoxide were purchased in cylinders and were of a purity greater than 99 per cent. Carbon monoxide was made by dropping commercial formic acid into warm sulfuric acid and purifying the evolved gas by scrubbing

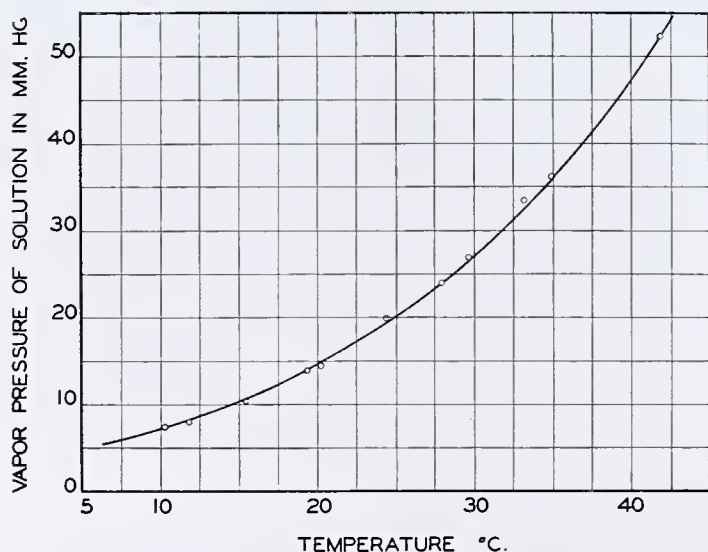


FIGURE 1. VAPOR PRESSURE OF CONFINING LIQUID



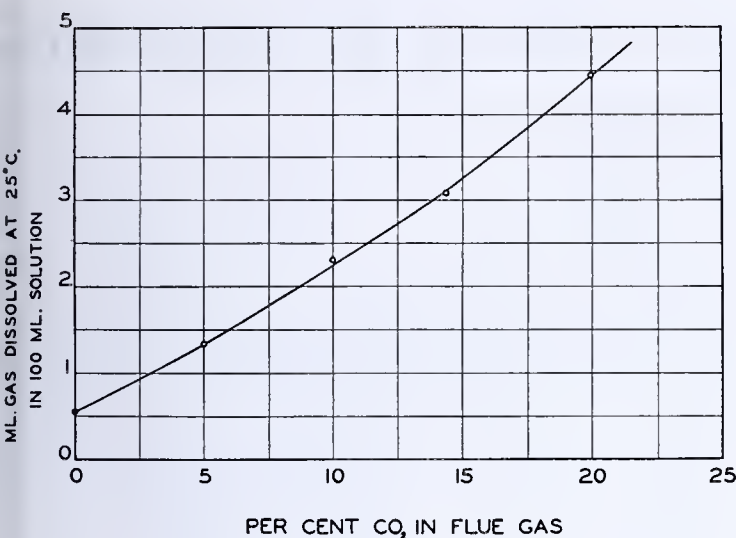


FIGURE 2. SOLUBILITY OF FLUE GAS

with caustic solution. The mixed gases were prepared by the use of the mine-air buret. Definite volumes of the gases measured in the buret were passed into a gas-sampling bulb over mercury and the contents of the bulb were thoroughly mixed by passing them back and forth between the buret and the gas bulb. The solubility of the mixture was determined in the same manner as the pure gases.

TABLE I. SOLUBILITIES OF GASES IN ACID SODIUM SULFATE SOLUTION

(Temperature 25° C., partial pressure of gas 760 mm.)

Gas	Volume of Solution Ml.	Gas Dissolved		Bunsen Coefficient <sup>b</sup>
		Ml.	Ml./ml. soln. <sup>a</sup>	
SO <sub>2</sub>	9.54	131.2		
	24.54	329.2	13.6	12.5
CO <sub>2</sub>	49.54	13.40	0.270	0.247
	49.54	13.40		
N <sub>2</sub> O	49.54	7.88	0.159	0.146
	49.54	7.90		
C <sub>2</sub> H <sub>2</sub>	49.54	17.01	0.343	0.324
	49.54	16.98		
C <sub>2</sub> H <sub>4</sub>	49.54	1.19	0.024	0.022
	49.54	1.19		
CH <sub>4</sub>	49.54	0.47	0.0093	0.0085
	49.54	0.45		
C <sub>2</sub> H <sub>6</sub>	49.54	0.54	0.0108	0.0099
	49.54	0.53		
H <sub>2</sub>	49.54	0.37	0.0073	0.0067
	99.54	0.72		
CO	99.54	0.39	0.0039	0.0036
	99.54	0.38		
O <sub>2</sub>	49.54	0.44	0.0089	0.0081
	49.54	0.44		
N <sub>2</sub>	99.54	0.50	0.0049	0.0045
	99.54	0.48		

<sup>a</sup> Milliliters of gas at 25° C., partial pressure of 760 mm., dissolved in 1 ml. of solution at 25° C.

<sup>b</sup> Milliliters of gas, corrected to 0° C., partial pressure of gas 760 mm., dissolved in 1 ml. of solution at 25° C.

The results have been expressed in terms of the milliliters of gas at 25° C. at a partial pressure of 760 mm. dissolved per milliliter of solution at 25°, and in terms of the Bunsen absorption coefficient ( $\alpha$ ) the volume of gas (corrected to 0° and 760 mm.) which, at the temperature of the experiment, is dissolved in one volume of the solvent when the partial pressure of the gas is 760 mm. The data and results for single gases are given in Table I.

### Solubilities of Mixed Gases

The solubilities of single gases are of little value in themselves, but give the necessary data from which the solubilities of gas mixtures may be calculated by Henry's law. In order to give a check on such calculations, the solubilities of various gas mixtures were determined, and are given in Table II.

Flue gas is one of the most commonly analyzed gases. Its carbon dioxide has a high solubility while carbon monoxide, oxygen, and nitrogen have low and similar solubilities. A change in the relative concentration of the latter three gases will produce only a negligible effect on the total solubility of the gas, as the solubility is almost entirely dependent on the carbon dioxide concentration. Because of this, varying concentrations of air and carbon dioxide were taken as representative flue-gas samples and their solubilities were determined. The results are shown in Figure 2, from which the solubility of a flue gas sample may be found if the carbon dioxide concentration is known.

TABLE II. SOLUBILITIES OF MIXED GASES

Gas %	Volume of Solution Ml.	Gas Dissolved		Bunsen Coefficient <sup>b</sup>
		Ml.	Ml./ml. soln. <sup>a</sup>	
Air	99.54	0.51		
	49.54	0.27	0.0053	0.0049
CO <sub>2</sub> 5	49.54	0.67	0.0135	0.0124
	49.54	0.67		
CO <sub>2</sub> 10	49.54	1.17	0.0235	0.0215
	49.54	1.16		
CO <sub>2</sub> 14.5	49.54	1.53	0.0310	0.0284
	49.54	1.54		
O <sub>2</sub> 6.1	49.54	1.54		
	49.54	1.54		
N <sub>2</sub> 79.4	49.54	2.21	0.0447	0.0410
	49.54	2.22		
CO <sub>2</sub> 20	49.54	2.21	0.0447	0.0410
	49.54	2.22		
CH <sub>4</sub> 40.3	49.54	2.80	0.056	0.0513
	49.54	2.75		
C <sub>2</sub> H <sub>4</sub> 39.9	49.54	2.75		
	49.54	2.75		
C <sub>2</sub> H <sub>2</sub> 19.8	49.54	2.75		
	49.54	2.75		

<sup>a</sup> Milliliters of gas at 25° C., partial pressure of 760 mm., dissolved in 1 ml. of solution at 25° C.

<sup>b</sup> Milliliters of gas, corrected to 0° C., partial pressure of gas 760 mm., dissolved in 1 ml. of solution at 25° C.

If the approximate form of Henry's law is used,  $p = KC$ , the solubility of gas mixtures may be calculated. The results found for the less soluble gases are very good, as the calculation of the solubility of air shows. Using the values for oxygen and nitrogen in Table I, the solubility of air is calculated to be 0.00525 ml. per ml. of solution, compared to the experimental value 0.0053 ml., which is within the experimental accuracy of the determination. Values calculated for the flue-gas compositions given in Table II show wider deviation due to the increased solubility of the carbon dioxide. In general, the more soluble the gas, the greater is its deviation from Henry's law. Thus, the calculated solubility of the hydrocarbon mixture of methane, ethylene, and acetylene is 0.0764 ml. per ml. of solution, compared to the experimental value 0.056 ml. The error is due to the decreased solubility of the acetylene under reduced partial pressure, as acetylene is next below sulfur dioxide in the order of solubility.

### Discussion

The results given in Tables I and II for carbon dioxide, acetylene, and mixed gases are accurate to 0.005 ml. in values for solubility or Bunsen coefficient. For sulfur dioxide, because of the high solubility, results are accurate to 0.5 ml.; for the other gases, an accuracy of 0.001 ml. is attained.

A comparison of these results with those of Kobe and Williams (1) for carbon dioxide shows a slight difference in values—0.247 compared to 0.242. This difference is due to difference in the concentration of the solution used and in the amount of sulfuric acid added. The true vapor pressure of the solution was used in this work, whereas previously it was assumed to be that of water.

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# Determination of Camphor in Alcoholic Solutions

## Dinitrophenylhydrazine Method

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IN AN INVESTIGATION of various methods for determining camphor in spirits and liniments, the dinitrophenylhydrazine reagent suggested by Brady (1), Fernandez and co-workers (2, 3), and Hampshire and Page (4) was used. After trying a number of experiments, the authors were informed that a modified dinitrophenylhydrazine method, in which 5 cc. of the spirit were used, was to be adopted as official in the U. S. Pharmacopœia XI. A number of experiments with the Hampshire and Page method and the suggested U. S. P. XI modification failed to give satisfactory results. Consequently work was undertaken to develop a modified procedure, which is presented below.

### Experimental

The first difficulty in both the Hampshire and Page and the modified U. S. P. XI methods was with the dinitrophenylhydrazine reagent, in which 1.5 grams of 2,4-dinitrophenylhydrazine are dissolved in a cooled mixture of 10 cc. of sulfuric acid and 10 cc. of water, and then sufficient water is added to make 100 cc. of solution. Fine crystals appeared soon after the reagent was diluted and cooled. A fine brown decomposition product was also formed after the solution had stood.

TABLE I. ANALYSIS OF SPIRIT OF CAMPHOR

Camphor Present %	Camphor Found—	
	U. S. P. XI method %	Hampshire and Page method %
5.0	8.02	8.96
5.0	7.26	6.87
5.0	8.14	7.19
10.0	7.24	13.31
10.0	8.00	10.92
10.0	7.21	11.38
15.0	11.44	14.47
15.0	8.14	14.43
15.0	12.11	14.74

A series of samples of spirit of camphor, prepared from camphors obtained from different sources, was carefully made to contain exactly 5.0, 7.5, 10.0, 12.5, and 15.0 grams of camphor in each 100 cc. of solution. The official 95 per cent alcohol was used in making these solutions. The U. S. P. XI was followed in the analysis of 5-cc. amounts of the different spirits. After the mixture had been refluxed, 200 cc. of 1 to 50 sulfuric acid were added, and the mixture was allowed to stand 24 hours. At the end of this period of time in many cases, especially when the spirits contained less than 10 per cent of camphor, numberless small, star-shaped crystals of dinitrophenylhydrazine which could not be separated from the hydrazone formed in the mixture. This condition, of course, caused some of the results to be high, especially in the lower percentage of camphor. With the spirits containing 10 per cent or more of camphor, a greater amount of the phenylhydrazine was used up, and therefore fewer crystals separated out. The lower results were caused by the sublimation of some of the camphor. Similar results were obtained with the Hampshire and Page method (Table I).

After completing the heating process, the authors diluted the mixture with various strengths of sulfuric acid, and discovered that 200 cc. of sulfuric acid (3 to 100) would prevent the crystallization of the dinitrophenylhydrazine. This change means that 13.5 cc. instead of 11.5 cc. of sulfuric acid (96 per cent) were present in each reaction mixture after

dilution. The amount of acid in the method of Hampshire and Page was equivalent to about 9.5 cc.

Later, the determination was found to be equally accurate when all the sulfuric acid was added to the reagent test solution, and this addition of acid had the added advantages that very little decomposition took place in the test solution on standing, and that the crystallization of the dinitrophenylhydrazine was reduced to a minimum. Experiments have shown that this modified reagent can be preserved for several weeks.

TABLE II. EFFECT OF ADDED SULFURIC ACID

Camphor Present %	Camphor Found—	
	U. S. P. XI method %	Hampshire and Page method %
5.0	4.45	4.86
5.0	4.20	4.78
5.0	4.39	4.83
10.0	7.74	9.73
10.0	7.44	9.68
10.0	7.23	9.78
15.0	8.81	14.44
15.0	8.69	14.55
15.0	8.65	14.51

By using this new test reagent, a number of determinations were made of different samples of spirit of camphor and gave results which were equivalent to less than the theoretical amounts of camphor (Table II).

The low results in the U. S. P. method (modified by adding more sulfuric acid to prevent the precipitation of the phenylhydrazine) were explained by the fact that a considerable quantity of camphor sublimed in the neck of the flask and in the reflux condenser during the heating process; consequently this camphor was never converted to the hydrazone. In order to overcome this difficulty with the modified U. S. P. method, various amounts of alcohol were added to the reaction mixture; the alcoholic vapors condensed and ran down the sides of the condenser and flask and thus washed any sublimed camphor back into the reaction mixture. The optimum amount of alcohol was found to be 15 cc. (Table III). With more than this amount of alcohol, some of the hydrazone formed was dissolved. All determinations reported below use the new reagent, with added amounts of alcohol.

The U. S. P. XI, through a typographical error, recommends the use of 25 cc. of spirit. With this amount of 10 per cent camphor solution, a number of determinations were made, and the maximum amount of camphor found was 3.45 per cent. Not enough dinitrophenylhydrazine is present in the

TABLE III. EFFECT OF ADDING ALCOHOL

Camphor Present	Alcohol Added							
	None	5 cc.	10 cc.	15 cc.	20 cc.	25 cc.	35 cc.	50 cc.
	Camphor Found— 5-Cc. Sample							
%	%	%	%	%	%	%	%	%
10.0	7.74	9.12	9.59	9.68	9.41	9.55	9.58	..
10.0	7.74	9.06	9.57	9.75	9.72	9.44	9.33	..
10.0	7.23	9.34	9.68	9.73	9.66	9.68	9.65	..
15.0	8.72	13.25	14.50	14.54	14.55	14.60	14.62	..
2-Cc. Sample								
5.0	4.45	4.81	4.88	4.90	..	4.78	..	4.37
7.5	6.39	7.19	7.37	7.40	..	7.36	..	6.78
10.0	8.59	9.47	9.79	9.82	..	9.79	..	9.11
10.0	8.41	9.43	9.83	9.80	..	9.75	..	9.15
15.0	10.14	13.99	14.65	14.72	..	14.60	..	14.33



TABLE IV. EFFECT OF VARIATION OF TIME OF HEATING MIXTURE								
Camphor Present %	Camphor Found (2-cc. samples)							
	1 hour	2 hours	3 hours	4 hours	5 hours	6 hours	9 hours	
5	4.45	4.85	4.92	4.90	4.92	4.95	4.90	
10	8.50	9.66	9.79	9.82	9.80	9.84	9.79	
15	12.33	13.90	14.63	14.76	14.75	14.80	14.75	
15	12.34	13.63	14.49	14.63	14.63	14.78	14.89	

TABLE V. EFFECT OF VARIATION OF TIME OF STANDING					
Camphor Present %	Camphor Found (2-cc. samples)				
	0 hour	24 hours	48 hours	96 hours	
5	4.83	4.91	4.94	4.90	
10	9.61	9.84	9.74	9.73	
10	9.78	9.86	9.82	9.80	
15	14.58	14.70	14.75	14.68	
15	14.63	14.63	14.69	14.73	

reagent to cause all the camphor to react when such a large sample is used.

In all the determinations where 5-cc. amounts were used, results were slightly below the theoretical values. The amount of spirit used in a determination was therefore reduced from 5 to 2 cc. Different amounts of added alcohol were tried. The optimum amount was 15 cc. with both 2-cc. and 5-cc. samples, and in all determinations reported below, 15 cc. of alcohol were added. When 2-cc. samples were used, the results obtained were somewhat nearer those of the theoretical value, especially with the spirit containing 10 per cent or more of camphor, than when 5-cc. samples were used (Table III).

Experiments were conducted next to discover whether or not the length of time of heating had any effect on the determination. The most efficient time seemed to be between 3 and 4 hours. Less than 3 hours' heating gave results which were considerably too low; and more than 4 hours' heating did not give results much higher than those obtained after 4 hours' heating (Table IV). More uniform results seemed to be obtained when the flask containing the reaction mixture was immersed completely in the water during the heating process.

Variations of the time of standing after the mixture was diluted were studied (Table V). If the mixture was filtered immediately after dilution, low, nonuniform results were obtained. If the mixtures stood longer than 24 hours, the results were approximately the same as those at the end of 24 hours.

TABLE VI. EFFECT OF VARYING QUANTITIES OF 2,4-DINITRO-PHENYLHYDRAZINE REAGENT					
Camphor Present %	2,4-Dinitrophenylhydrazine Reagent				
	17.4 cc.	20 cc.	40 cc.	75 cc.	150 cc.
	Camphor Found (2-cc. samples)				
	%	%	%	%	%
5	3.96	4.10	4.67	4.90	4.89
10	6.25	6.99	9.23	9.80	9.74
15				14.70	14.79

A series of experiments was conducted to determine the effect of varying quantities of 2,4-dinitrophenylhydrazine reagent. When 17.4 cc. of the reagent solution were used, the amount of hydrazine present was about equivalent to the amount of camphor in 2 cc. of a 10 per cent spirit. The results of this study (Table VI) indicate that the reagent must be present in substantial excess, but that there is evidently a

limit to the excess that is necessary, as shown by the results with 150 cc. of the reagent solution.

The consistently low results might have been caused by the slight solubility of the hydrazone in the reaction mixture. The theoretical amounts of hydrazone which would be formed from the camphor in 2-cc. amounts of the 10.00 and 20.00 per cent spirit were calculated. These amounts of hydrazone were placed in separate flasks and sulfuric acid, alcohol, water, and excess dinitrophenylhydrazine were added in the same amounts which would be present in the reaction flask after being heated in the modified official assay. The mixture was treated exactly as in the modified official determination. The results obtained (Table VII) show that very little solubility takes place. The solubility of the hydrazone was tried also in the alcohol-water-acid mixture without the dinitrophenylhydrazine reagent (Table VII). The results of these latter experiments showed a greater solubility than that obtained when the excess dinitrophenylhydrazine was present.

TABLE VII. SOLUBILITIES OF CAMPHOR DINITROPHENYLHYDRAZONE						
Detn. No.	Reagent Added			No Reagent Added		
	Hydrazone Added Gram	Hydrazone Recovered Gram	Calculated loss or gain as camphor G./100 cc.	Hydrazone Added Gram	Hydrazone Recovered Gram	Calculated loss as camphor G./100 cc.
1	0.4406	0.4412	+0.01	0.4332	0.4076	-0.59
2	0.4379	0.4378	+0.00	0.4416	0.4241	-0.40
3	0.4357	0.4366	+0.02	0.4379	0.4191	-0.43
4	0.8674	0.8645	-0.07	0.8830	0.8606	-0.51
5	0.8750	0.8707	-0.10	0.8742	0.8509	-0.53
6	0.8700	0.8667	-0.08	0.8648	0.8439	-0.48

The effect of temperature and time of heating were tried on different samples of the hydrazone. The results (Table VIII) show that the time and temperature of heating within reasonable limits have little effect on the hydrazone.

A number of blank determinations were tried. In these experiments, the reaction flask contained all the reagents except the spirit of camphor. The process was completed and a slight precipitate was obtained. The amounts of these precipitates, when calculated as percentage of camphor never amounted, however, to as much as 0.1 per cent.

TABLE VIII. EFFECT OF HEAT ON CAMPHOR 2,4-DINITRO-PHENYLHYDRAZONE				
Continuous Heating Hours	Temperature ° C.	Weight in Grams		
		No. 1	No. 2	No. 3
Series 1				
0	...	1.2749	1.2701	1.2670
48	100	1.2737	1.2692	1.2661
96	100	1.2735	1.2690	1.2660
120	100	1.2736	1.2690	1.2655
Series 2				
0	...	0.2168	0.4313	0.4317
147	94	0.2166	0.4311	0.4317
210	98	0.2163	0.4311	0.4314
356	100	0.2161	0.4307	0.4311
623	109	0.2153	0.4301	0.4306
664	110	0.2151	0.4299	0.4304

When this communication was first submitted for publication, a copy was sent to the chairman of the subcommittee on organic chemicals of the U. S. Pharmacopœia (5), who did not agree with a number of the authors' contentions. He found no indication of camphor's subliming when the mixture without added alcohol was refluxed on a steam bath, and he found the U. S. P. XI method without modification to give results which ranged from 98.2 to 99.02 per cent recovery. This subcommittee reported a number of experiments on the determination of camphor.

The reviewer of this paper, however, repeated some of the authors' experiments and found that their modification gave results equivalent to 96.12 to 96.36 per cent recovery with 10 per cent camphor solutions. His results with the U. S. P. XI method (5-cc. sample) confirmed the authors' and were very low—71.7 to 79.1 per cent recovery.



In view of the above-mentioned discrepancies, several samples of spirit were submitted to a number of analysts (Table IX). Analysts 1, 2, 3, and 4 were expert drug chemists. Analyst number 5 was a student, whose first ten results show an average of 9.69 per cent of camphor. However, after running several additional lots, this same operator averaged 9.81 per cent.

All experiments indicate that the low results are due to impurities in the camphor, to an incomplete reaction, or to decomposition of the hydrazone rather than to the solubility of the hydrazone. Since the average recovery amounts to about 98 per cent, it is suggested that 0.2 per cent should be added to the results obtained in each determination to correct the low results.

### Proposed Method

The proposed modification may be given in detail as follows:

Accurately measure 2 cc. of spirit of camphor into a 300-cc. Erlenmeyer flask containing 15 cc. of alcohol, and add 75 cc. of dinitrophenylhydrazine reagent solution. Connect the flask with a reflux condenser, and heat the flask for 4 hours by immersing it in actively boiling water. Allow the mixture to cool, add 200 cc. of distilled water, and set aside for 24 hours. Transfer the precipitate to a previously dried and weighed Gooch crucible, and wash with small portions of cold distilled water until the washings are no longer acid to litmus paper. Continue the suction until the excess water is removed, dry the crucible, and precipitate to constant weight at 100° C. The weight of the precipitate multiplied by 22.9 equals the weight of camphor in 100 cc. of spirit of camphor. To correct the low results given by the method, add to the percentage of camphor found 0.2 per cent.

The dinitrophenylhydrazine reagent solution is prepared in the following manner:

Dissolve 3.75 grams of 2,4-dinitrophenylhydrazine in a warm mixture of 45 cc. of concentrated sulfuric acid and 45 cc. of dis-

TABLE IX. RESULTS OBTAINED BY DIFFERENT ANALYSTS WITH THE PROPOSED METHOD  
(10% Camphor Solution)

Sample No.	Analyst 1	Analyst 2	Analyst 3	Analyst 4	Analyst 5 No experi- ence	Analyst 5 After ex- perience
1	9.78	9.79	9.74	9.89	9.62	9.85
2	9.84	9.81	9.77	9.83	9.74	9.81
3	9.75	9.85	9.83	9.80	9.80	9.79
4	9.65	9.78	9.75	9.77	9.62	9.88
5	9.78	9.78	9.76	9.87	9.56	9.85
6	9.79	9.75	9.73	9.82	9.60	9.84
7	9.69	9.84	9.76	9.84	9.69	9.80
8	9.86	9.83	9.80	9.79	9.66	9.83
9	9.71	9.76	9.79	9.88	9.80	9.71
10	9.92	9.81	9.77	9.82	9.78	9.74
Av.	9.78	9.80	9.77	9.83	9.69	9.81
Plus cor- rection of 0.2 per cent	9.98	10.00	9.97	10.03	9.89	10.01

tilled water. Cool the solution, and add enough distilled water to make the solution measure 250 cc. If necessary, filter the solution before using it.

A number of spirits made from synthetic camphor have been analyzed by the proposed modification. This study will be continued and reported later.

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RECEIVED April 10, 1936.

## Iodofluoride Method for the Determination of Copper

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IN A RECENT article (3) results of volumetric determinations of copper in a number of samples of cupric sulfide obtained by a so-called "iodofluoride" method were reported, as a modification of the procedure described by Crowell (1). In a discussion of the results it was stated that the iodofluoride method cannot be used when more than 0.15 gram of iron is present and that in all titrations the presence of a yellow color interfered with the sharpness of the end point. If one uses this modified procedure, in which bifluoride is added to the sulfuric acid solution of the sample without any addition of ammonia, the pH of the solution is about 1.1 instead of between 3 and 4, the region within which it is generally agreed that it is best to work. If, on the other hand, one uses the procedure of the authors of the present paper in which sufficient ammonia is added to produce a pH of 3.3 or somewhat above, not only are the end points white, sharp, and permanent but copper determinations in the presence of as much as 0.3 gram of iron and corresponding amounts of arsenic and arsenopyrite can be made with high accuracy and precision.

### Experimental Procedure

Except for the addition of thiocyanate, the steps are essentially the same as in the method previously reported (1).

The sample consisting of 0.3 to 0.4 gram of copper sulfide is weighed into a 250-cc. Erlenmeyer flask containing measured amounts of the impurities under investigation, 20 cc. of aqua regia and 10 cc. of 18 N sulfuric acid are added, and the reaction is allowed to proceed slowly until there is no evidence of free sulfur present. During this stage a small watch glass is placed over the mouth of the flask. The flask is then embedded in a steam-heated sand bath, the watch glass raised slightly, and the solution heated just below boiling until the point of incipient fuming is reached. Twenty cubic centimeters more of aqua regia are added, and the evaporation is continued and finally finished on a gas or electrically heated sand bath as soon as dense white fumes appear. To the solution are added 20 cc. of water and ammonia solution until a slight but distinctly recognizable odor of ammonia is obtained. Finally 1.5 grams of ammonium bifluoride are added, followed by iodide and titration with thio-sulfate with the addition of 2 grams of potassium thiocyanate near the end point.

Even in those runs in which the largest amounts of iron and of arsenic were present, 1.5 grams of bifluoride were found sufficient. When iron and manganese are present together, it is best to add the ammonia after the bifluoride (2). In such a case the proper amount of ammonia is determined by treating several samples in the same manner as those run for analysis, carrying the operation only to the point at which a distinct odor of ammonia is obtained. Blank runs on the copper sulfide are made, using the same procedure as that employed when impurities were present.

Table I shows results of analyses of several series of cupric sulfide samples in the presence of various impurities, using



TABLE I. ANALYSIS OF COPPER SULFIDE IN THE PRESENCE OF INTERFERING ELEMENTS

Impurity present Amount, gram	(The percentage of copper in the pure sulfide varied from 64.37 to 64.12.)							
	Fe 0.1	Fe 0.2	Fe 0.3	As 0.1-0.2	As 0.3	Fe + As Fe 0.1-0.2 As 0.1-0.2	Arsenopyrite 0.2	Arsenopyrite 0.3
Average deviation <sup>a</sup>	+0.04(7) <sup>b</sup>	-0.02(5)	-0.07(6)	-0.05(8)	-0.14(3)	-0.05(5)	0.00(5)	-0.11(4)
Maximum deviation <sup>a</sup>	+0.10	-0.07	-0.15	-0.14	-0.20	-0.06	+0.06	-0.23

<sup>a</sup> The deviations are percentage deviations from the per cent of copper obtained in the blank runs.  
<sup>b</sup> The numbers in parentheses refer to the number of determinations made.

the procedure just described. A greater variety of impurities and larger amounts are used than in the previous work (1).

The copper sulfide samples were obtained from a pound of the c. p. compound which had been finely ground and thoroughly mixed. The iron and arsenic impurities were supplied from solutions of ferric nitrate and arsenic acid. The arsenopyrite was prepared from a specimen of copper-free mineral.

The results indicate that by the procedure employed copper determinations can be made in the presence of as much as 0.3 gram of iron, 0.2 gram of arsenic, 0.2 gram each

of iron and arsenic together, and 0.2 gram of arsenopyrite with an error less than 0.1 per cent, and in the presence of as much as 0.3 gram of arsenic and 0.3 gram of arsenopyrite with an error less than 0.2 per cent.

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## Routine Determination of Low Chromium in Aluminum Alloy

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IN STEELS, chromium is most easily determined (2) by dissolving the steel in aqua regia, oxidizing the chromium with perchloric acid, and then titrating the chromic acid with ferrous sulfate. Solution of aluminum alloys takes place readily with aqua regia, but heating after treatment with perchloric acid results in the formation of an insoluble deposit which causes bumping. Oxidation of the chromium is incomplete.

When a mixture of phosphoric and perchloric acids is used as solvent for the aluminum alloys, solution is complete, and upon further heating the chromium is oxidized to chromic acid. Manganese, if present, is oxidized to the trivalent state; iron, copper, magnesium, and aluminum are without bearing on the results; and silicon is more or less held in solution.

The accepted methods for the determination of chromium are either the direct oxidation of the element in sulfuric acid solution by potassium permanganate, or by silver nitrate-persulfate (1). Both these methods have been used in steels, but are neither as rapid nor as easily handled as is the routine perchloric acid method when a large group of samples is involved. The same advantages of ease of solution, oxidation, and handling of the samples apply to the perchloric acid method for aluminum alloys.

### Proposed Method

Dissolve 1 gram of aluminum alloy in a 400-cc. covered beaker in a mixture of 10 cc. of 85 per cent phosphoric acid and 10 cc. of 70 per cent technical perchloric acid. If necessary, heat at about 120° C. until solution is complete. Move the beaker to a spot on the hot plate where the contents of the beaker will be heated to about 220° C. After the color change (yellow for chromium only, but brown for manganese and chromium together), heat about 5 minutes more. Remove from the heat, and cool somewhat with the cover partially removed. Dilute to 100 cc., add 5 cc. of hydrochloric acid (1 to 3), and boil out chlorine. Add 10 cc. of sulfuric acid (1 to 1), dilute to 100 cc., and cool to 25° C., or less. Titrate potentiometrically with ferrous sulfate (or other acceptable method). 1 cc. of 0.1 N  $\text{FeSO}_4 = 0.1738$  per cent Cr.

Readings were made to the nearest 0.1 cc. or 0.017 per cent chromium. As the oxidation of chromium is not complete, the ferrous sulfate may be standardized by adding chromium to a chromium-free aluminum sample. However, when a 0.3 per cent chromium sample is to be used, oxida-

tion to the extent of only 98 per cent of the chromium content involves no error.

Hydrochloric acid is added to the oxidized solution for the purpose of reducing the manganese to the bivalent stage, but need not be used if manganese is absent.

Titration performed above 25° C. give lower results.

TABLE I. CHROMIUM CONTENT

	Sample 53-S			
	0.21	0.22	0.22	0.23
Outside laboratory	0.21	0.22	0.21	0.22
Persulfate method <sup>a</sup>	0.23	0.23	0.23	0.24
Proposed method	0.26	0.25	0.25	0.25
Proposed method, Mn added				
	Sample 52-S			
	0.22	0.23	0.23	0.24
Outside laboratory	0.21	0.22	0.22	0.22
Persulfate method <sup>b</sup>	0.25	0.24	0.25	0.25
Proposed method	0.24	0.23	0.23	0.23
Outside contractor	0.23	0.25	0.25	0.25
Persulfate method <sup>a</sup>	0.24	0.24	0.25	0.24
Proposed method				

Approximate Composition

	Mn	Mg	Cu	Si	Fe	Al
53-S, %	0	1.1-1.4	0.01-0.02	0.5-0.7	0.15-0.19	97
52-S, %	0	2.3-2.8	0.01-0.03	0.1-0.16	0.16-0.20	97

<sup>a, b</sup> Results by O. Gates and A. Allison, respectively, Navy Laboratory, Munhall, Pa.

**PRECAUTIONS.** Solution of aluminum alloys in phosphoric-perchloric acids generates hydrogen; hence no gas flames should be lighted nearby. Aluminum powder containing grease should first be extracted with acetone, since concentrated perchloric acid rapidly oxidizes grease.

When aluminum powder is to be dissolved, the powder and reagent are heated on a steam bath, and removed when action starts. When the rapid action ceases the regular procedure is followed.

If powder and perchloric acid alone are used, partial solution takes place, but if the mixture is heated, the acid dehydrates and will vigorously attack any dry powder, possibly causing a mild explosion.

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RECEIVED September 6, 1937.



# Load-Versus-Compression Characteristics of Gelatins, Fibers, and Other Materials

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The qualities of gelatins, jellies, and similar materials are physically determined by gel strength, gel factor, yield point, elastic hysteresis, etc. The author has developed a precision apparatus with which it is possible to determine these characteristics with an exactness of four significant figures under reproducible conditions in a simple manner. The method

and the instrument lend themselves also to measurements of food products, greases, canned and cooked fruits and vegetables, and other plastic and semi-plastic materials. In many instances the universal gelometer effectively supplements findings obtained by plastometers, compressometers, elastometers, and stiffness testers.

GELATINS and glues are purchased substantially on the basis of their Bloom number—that is, the number of grams necessary to push a cylindrical plunger 12.75 mm. in diameter 4 mm. deep into a standard sample of gelatin (1). Gelatins of high gel strength require more weight (applied by shot loading) for that purpose, while softer gelatins require less shot. While the penetration of 4 mm. was chosen because in most instances, at the concentrations described in the original paper, no yielding occurs at penetrations as low as 4 mm., we have to go beyond that depth to investigate the yield point, the gel factor, and elastic hysteresis. Furthermore, because it has been found necessary not only to load the specimens but to observe their behavior at a systematic reduction of the load, shot loading has been found impractical.

Instruments of this type should be designed to give not only data as to penetrating properties, but such factors as elastic recovery, hysteresis phenomena, gel factor, and yield point, which cannot be practically determined with the Bloom gelometer. The gelometer described here, which has been used successfully in research and practice for several years,

makes possible the precise evaluation of all these factors in a reproducible manner, and does not conflict with patents that restrict the use of the Bloom gelometer. It is manufactured commercially.

## The Apparatus

The general physical principles of the apparatus are rather broad (1, 8). The apparatus consists substantially of a sensitive balance with a movable tare weight (Figure 1, right). A sample prepared under standard conditions is placed upon the pan of this scale and a plunger with a hard-rubber tip is depressed into it. The piston, with rack and pinion drive, vernier, and attached reading glass, is shown on the left side of Figure 1.

A load-versus-depression characteristic can be determined by depressing the plunger into the sample a given distance and moving the weights on the balance arm to bring the pointer back to zero. Stiffness as well as elastic recovery may be tested in this manner.

Additional agents such as glycerol, sodium benzoate, zinc sulfate, etc., influence the elastic recovery and elastic hysteresis.

## Determination of Gel Strength

The method is applicable not only to glues and gelatins, but also to rubber, biological matter, cheese, fruits, jellies, meat, gelatin desserts, textile fibers, canned food, ice cream, bread, and other baked products, mayonnaise, hard and soft gelatin capsules, and marshmallows. The recovery characteristics and their change with age, moisture content, and heat are particularly important for marshmallows. The drier, older, and harder the marshmallows are, the less good is their recovery.

Because the elastic recovery in the wet state and in the dry state has a definite relation, measurements of elastic recovery plastic deformation and elastic hysteresis are of considerable scientific and industrial importance. A shot-loading instrument does not readily permit the deduction of load and, therefore, the customary types of gelometers are useless for this purpose.

There is no such thing as an ideal texture, because in one instance a high stiffness is desirable whereas in another plastic

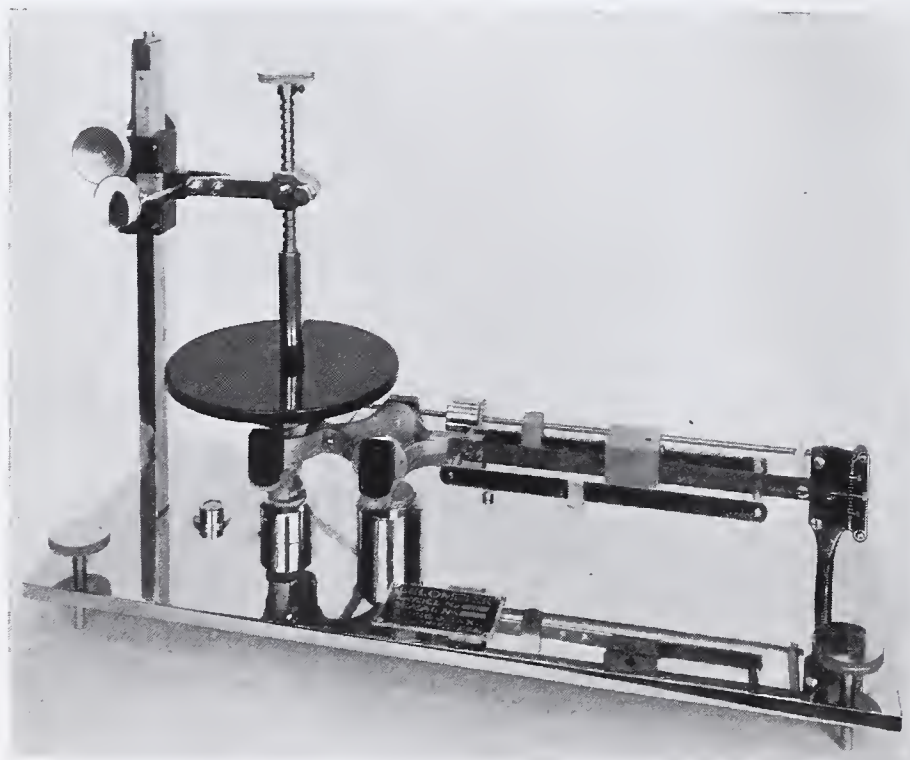


FIGURE 1



deformation and a high grade of elastic recovery are preferable. Specifications must be adapted to the requirements of the manufacturers of candy, marshmallows, and other food products.

Factors such as clarity in color, freedom from obnoxious odors, viscosity and gluing power (tackiness), surface friction and smoothness (3), swelling, hydrogen-ion concentration (10), ash, isoelectric point, etc., are also of importance in certain applications of gelatin.

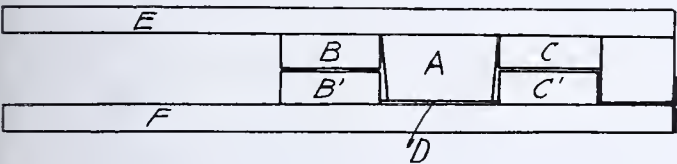


FIGURE 2

**THE SAMPLE.** In all instances, the samples must be prepared analogously and properly in order to get comparable conditions. With the great multitude of possible materials ranging from tooth paste to jello, it is not practical to give specifications for the preparation of each sample. Instead, specifications are presented as they apply to the measurement of gelatins, in order to get the same results as with the standard Bloom test (1).

**CONTAINER FOR JELLY.** The container recommended is an extra widemouthed bottle of the following specifications: capacity, 150 cc.; inside diameter of body, 59 mm.; outside diameter, 66 mm.; height over-all, 85 mm.; to take rubber stopper No. 9. Bottles should show a variation of not more than 1 mm. in average internal diameter from these dimensions. The tapered stopper is cut in half and the upper portion is perforated by plunging a red-hot, 2.5-cm. (1-inch) rod through it at the center. The upper half of the stopper is used to obtain a snug fit in the neck of the bottle and the air vent prevents the stopper from being blown out during the melting and heating of the sample. The containers and stoppers must be clean and dry. To cut the rubber stopper in half, a tool has been developed by Miner D. Given, of the Eastman Gelatine Corporation (Figure 2): The rubber stopper, A, is inserted between two holding bars, B and C, and depressed by a bar, D, with the aid of the rollers, E and F. The rubber stopper, held rigid in this manner, is cut easily and straight with a knife that has been wet with caustic soda.

Instead of making a 2.5-cm. (1-inch) hole, a small wire rod or knitting needle, 2 mm. in diameter, may be heated and plunged hot through the center of the stopper. This provides a small air vent and facilitates heating and lifting the stopper after heating the sample. This smaller hole is a better protection against impurities contaminating the surface of the gelatin, and guards against undue evaporation of the water in the sample while heating. Moreover, it can be covered easily with the finger and the liquid hot gelatin tilted until there are no air bubbles on top of the gelatin.

Violent agitation of the hot solution is to be avoided because it causes damage in the viscosity, and in some cases persistent lumps are formed which may interfere with the subsequent jelly test. It is important that the plunger rest upon a clean gelatin surface, not upon jelled and frozen foam.

**SAMPLING AND PREPARATION OF SAMPLE.** A grab sample of ground glue or equivalent in the ratio of 28 grams per 45 kg. (1 ounce per 100 pounds) is taken at random from not less than 20 per cent of the containers. The total number of samples so taken should not be less than ten; when the number of containers in the shipment is less than 10, a sample should be taken from each container.

A sample of sheet, flake glue, etc., is taken as for ground glue, except that in case of large lots the portion taken from each container is reduced proportionately so that the total sample does not exceed 4.5 kg. (10 pounds).

The entire sample is then ground to at least 4-mesh, or finer if it appears necessary, so as to minimize weighing errors and to shorten the soaking period.

The entire ground sample is thoroughly mixed and quartered down until reduced to two 454-gram (1-pound) samples, which are placed in air-tight containers. One of these is used for test and the other held as a reserve sample.

**CONCENTRATION.** For 105 cc. of distilled water 7.5 grams of gelatin are used—a concentration of 1 to 14. This is called the gelatin scale. For glues, which have a lower gel strength, 15 grams of glue are dissolved in 105 cc. of water—concentration of 1 to 7. This is called the glue scale. An automatic pipet with a three-way stopcock may be used to deliver the water correctly in routine work.

The dissolved sample in the tightly stoppered container is allowed to cool to 45° C., preferably in a water bath. The finger is then placed over the perforation in the stopper and the container is inverted several times to mix in the water that has condensed on the walls of the bottle and the under side of the stopper. The containers are then placed in a constant-temperature chill bath for not less than 16 nor more than 18 hours at 10° ± 0.1° C., taking care not to insert too many samples to maintain the temperature capacity of the equipment. The temperature variation and reasonable agitation of the chill bath are important. Unless the batch controls the temperature within the limits prescribed, it will be necessary to use "standards" and thus make relative, not absolute, tests. Thermostatic recording and regulating equipment may be used.

**TECHNIC OF MEASUREMENT.** After the sample has been made a beaker of cold water, which has as near as possible a temperature of 10° C., is placed upon the pan of the balance. The plunger is inserted into this chill bath and left there for 2 minutes, so as to be reasonably close to the temperature of the testing specimen.

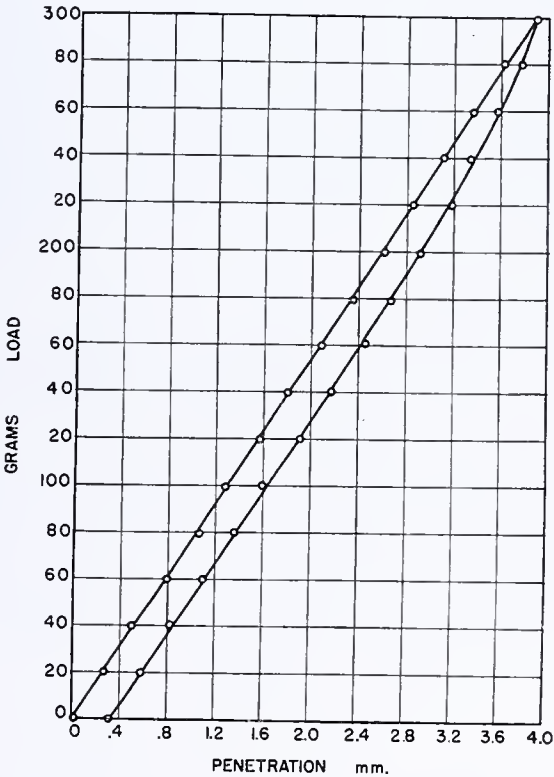


FIGURE 3

The tip of the plunger is made of hard rubber in order to reduce the thermal conductivity. After this tip has been chilled for 2 minutes, if the samples are brought in reasonably fast, the temperature of the plunger surface is the same as that of the sample to be tested. The plunger is now dried with a towel. (Between samples the plunger is cleaned.) The arm on the rack and pinion drive is lifted so that the reading on the vernier scale is exactly zero, and the plunger is lowered first with the acme screw only (at the right side of the arm). By turning the knob on top of the screw, the plunger can be lifted or lowered until it just touches the surface of the test sample in the bottle. This can be ascertained with great precision by watching the pointer at the right side of the scale, which shows the motion of the pan about four times enlarged.

Before lowering the plunger, a sample contained in the water bath is calibrated by the tare weight (the metal cylinder running upon a screw in back of the scale). By calibrating with the scale pointing at zero and all weights in zero position, readings taken will be direct load-versus-penetration readings, and no subtraction has to be made for the tare.

After the sample has been brought into position, the acme screw is clamped tightly with a clamp in front of its bearing. All



the motion applied to the plunger must now come from the rack and pinion drive. The drive is now lowered until the vernier reads exactly 0.40 cm. Because the plunger depresses the sample, the pointer at the right side of the scale points upward. The weight in grams necessary to bring the pointer back to zero if the standard plunger is depressed 4 mm. into the gelatin sample prepared as above is called the Bloom number.

This standard depression can be read with the precision of four significant figures. The maintenance of this constant depth is more precise than a gap with contact points that may arc under the influence of electric current and burn out, as in some apparatus. Furthermore, the weight can be read to 0.1 gram, which is one more significant figure than the commercial types of gelometers give. The new gelometer is independent of electric batteries and clean and dry shot. This instrument, therefore, gives at least one decimal fraction more than the standard testing instrument, both in the precision of the load and in depth readings.

Several important characteristics can be determined readily with the new gelometer which cannot be ascertained in a practical manner with previous instruments (3, 5).

### Elastic Hysteresis

Weight cannot only be applied with the gelometer described above, but can be reduced after load application has taken place. Then, by lifting the plunger point by point, the elastic recovery of the product investigated can be measured. Some plastic deformation does take place, but the total amount varies for different materials, and is not necessarily proportionate to gel strength. In other words, in determining only the penetration for 4 mm., we have no means of predicting whether the jellying substance will recover elastically or will remain plastically deformed.

Figure 3 shows a hysteresis loop determined by first increasing the weight and measuring the penetration which brought the balance back to zero, and thereafter decreasing the weight again. The area of this loop is proportionate to the internal distributed forces that counteract a recovery of the sample to zero position. Here a permanent deformation of 0.03 cm. has been effected. Moreover, the difference between load applied and load removed per unit of penetration is small at the beginning and increases thereafter. At 3.2-mm. depression a load difference of 20 grams exists between the ascending and the descending branch of the characteristic. At a depression of 0.60 cm., however, this weight difference has

increased to 30 grams, which is practically maintained until zero load.

### Measurements on Staple Fiber

While the methods described above apply primarily to the evaluation of plastic and semiplastic materials, the apparatus lends itself also to the investigation of fibrous materials such as wool, and staple fiber in bulk, and fabrics (4, 6).

For making tests for resiliency and elastic recovery, load-versus-compression characteristics were taken on a standard sample (Figure 4). First a plunger 1.27 cm. (0.5 inch) in diameter is attached on top of a standard sample first of spun rayon and then of synthetic wool, weighing 16.9 grams each. As we are working within one test jar and are dealing with identical quantities, the only variable in the load-versus-compression characteristic between the two is the elasticity and elastic recovery.

After the jar with contents is tared out, the circular plunger 1.27 cm. (0.5 inch) in diameter is lowered with the acme screw until it touches the surface of the sample. Weight is then moved out upon the balance arm and the plunger is lowered until the pointer of the scale again indicates zero. By this means we arrive at the weight necessary to produce a given compression, as indicated by Table I.

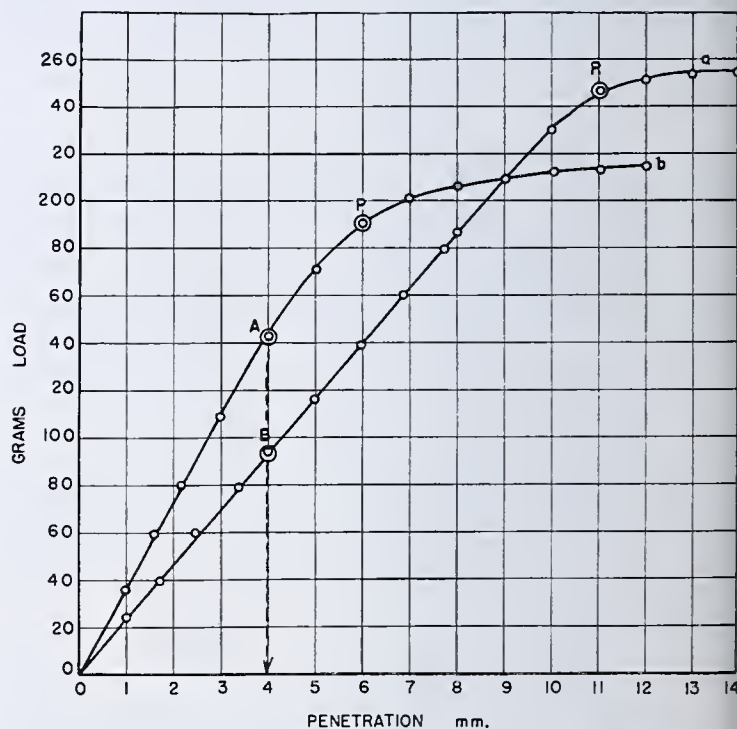


FIGURE 5

If, instead of the staple material, we had had a 100 per cent elastic spring in the jar, this spring would have returned along the curve through which it was depressed first. On the other hand, if we were dealing with 100 per cent plastic body, the elastic recovery would have been zero or a permanent plastic deformation would have been achieved that would be identical to the maximum depression made.

Between the extremes of 100 per cent elastic recovery and 100 per cent plastic deformation, there is the relative elastic recovery of the materials compared (Figure 4). Materials are the more elastic, the narrower the area of the loop. The relative characteristics of elasticity are inversely proportionate to the area of the hysteresis loops.

The elastic recovery of the synthetic wool is between two and three times as good as that of the original spun rayon used in comparison, particularly in those areas in which characteristic stresses during actual operation occurred. At 200 grams compression the diameter of the synthetic wool loop is 1.6 divisions, while the spun rayon loop is 3.0 divisions.

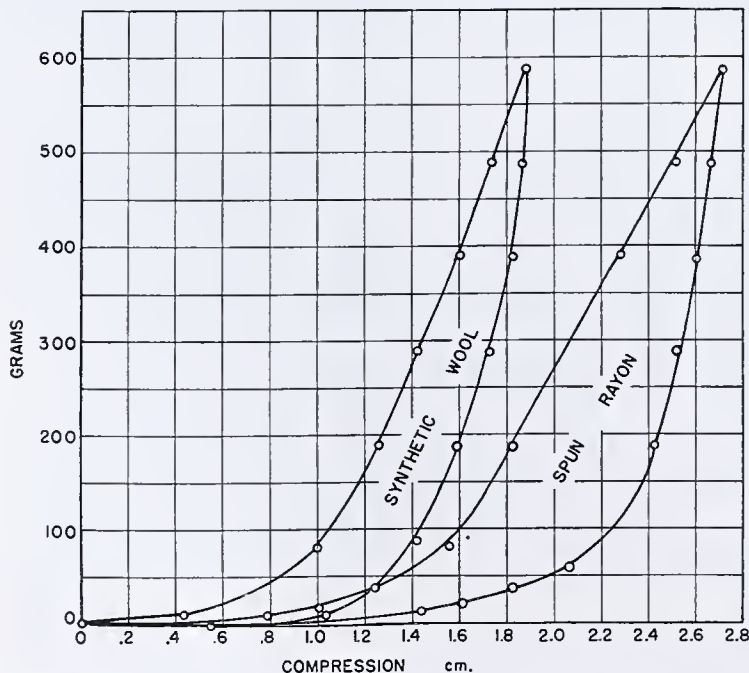


FIGURE 4



TABLE I. LOAD-VERSUS-COMPRESSION CHARACTERISTICS

Filled with Spun Rayon		Filled with a New Type of Synthetic Wool	
Grams	Compression Cm.	Grams	Compression Cm.
0	0.0	0	0.0
10	0.79	10	0.44
20	1.1	20	0.68
40	1.24	60	0.90
60	1.35	80	1.00
80	1.47	190	1.28
190	1.82	290	1.42
290	2.09	390	1.62
390	2.28	490	1.74
490	2.53	590	1.89
590	2.71		
490	2.67	490	1.86
390	2.61	390	1.83
290	2.52	290	1.73
190	2.42	190	1.59
90	2.22	90	1.43
60	2.07	60	1.35
40	1.83	40	1.26
20	1.61	20	1.24
10	1.45	10	1.03
0	0.94	0	0.55

The same principle of measurement applies to many other substances. Because of its inherent simplicity, accuracy, and wide range, the new gelometer is applicable in practically all instances where various forms of plastometers have been used heretofore, particularly in measurements on rubber and rubber compounds, synthetic resins in combination with textiles such as crush-proofing tests for urea-formaldehyde-treated velveteens and rugs (instead of compressometers), and in taking complete load-versus-compression characteristics on folded or rolled sheetlike materials such as paper, cloth, and metal foils. In this latter instance the universal gelometer nicely supplements the results obtained with the stiffness tester. The apparatus can also be adapted readily for tests heretofore taken with the elastometer.

### Elastic Recovery

Instead of taking complete hysteresis curves, it is possible merely to determine the elastic recovery which a gelatin or other material is capable of sustaining after a certain load has been applied during a given time. In many instances this simplified measurement will give the desired first-hand information about the forces of elastic recovery.

Care should be taken to work with the same total amount of time in all instances of comparative measurements; otherwise the time factor influences the readings. Deformation and recovery are not instantaneous; a small load applied over a considerable length of time may produce more permanent deformation than a comparatively larger load applied for a rather short time. Questions of rheological nature (such as plastic flow) enter here.

The technic for such determinations is to make the standard specimen and calibrate it with the tare weight upon the scale, then lower the plunger until it touches the surface of the gelatin. A given weight—for instance, 100 grams—is applied for one minute and the plunger is lowered with the rack and pinion drive until the pointer at the right hand of the scale again indicates zero. The depression is now read on the vernier.

The weight of the balance is returned to zero and the plunger is lifted on the rack and pinion drive until the hand of the scale again points to zero. Under these conditions the plunger will not return to zero but a certain amount of impression will remain permanent. It is read directly on the vernier.

The recovery of jellies to the original form in which they were cast will be the more complete the better the recovery of gelatin test specimens after removal of the load.

### Yield Point

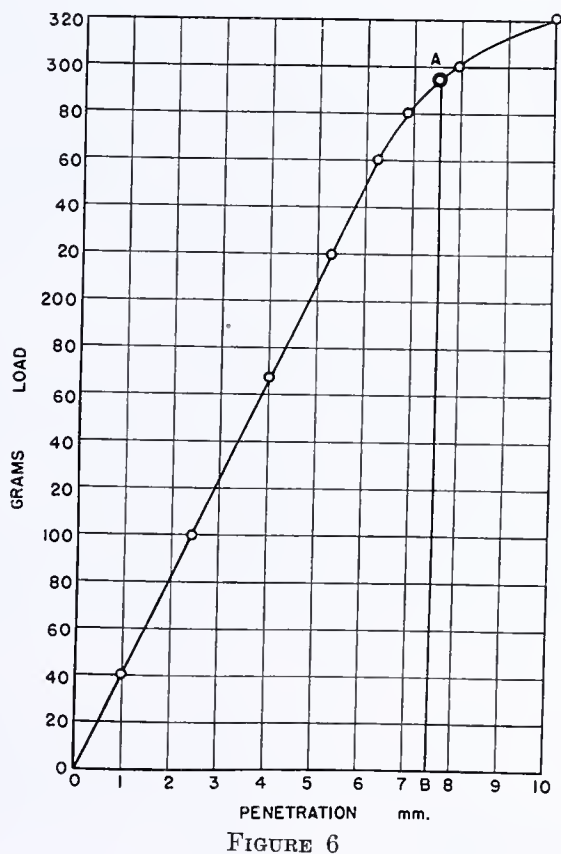
The yield point appears at the point of the load-versus-penetration curve where, without further addition of load,

the plunger penetrates into the material. At this point the elastic limit has been trespassed. The yield point and subsequent slope of the load-penetration characteristic are influenced by the mixture of compounds ordinarily called gelatin.

The elastic limit is not necessarily influenced by the Bloom number of the gelatin. Everything else being equal, the yield point at a comparatively low stiffness number may lie higher. In other words, the maximum stress to which such a jelly may be subjected and still recover completely is not necessarily dependent upon the Bloom number. Figure 5 will make this clear. In this instance curve *b* has a higher Bloom number as shown by a load of 142 grams at 4-mm. penetration (point *A*), yet the maximum load which this material can sustain lies at 190 grams (point *P*).

On the other hand, the comparatively softer material represented by curve *a*, the Bloom number of which is 46 grams lower (point *B*), yields at a substantially higher load—namely, 246 grams (point *R*). While *b* will give suitable data for gelatins where stiffness only is desired, curve *A* is preferable for jellies where the desirable characteristic is resistance against final deformation. A certain amount of elastic give is possible which can raise the yield point substantially.

The question of yield point is also important from a different viewpoint. Comparative measurements on which a report is to be made shortly show that the yield point stays in a certain relation to the maximum tensile strength to which the gelatin films or materials covered with gelatin films can be subjected. This is of particular interest in the paper, textile, leather, and photographic industries.



It is imperative that means for evaluating the physical characteristics of jellies shall have a range wide enough to continue with the measurements until the final break. For this purpose facilities for penetration in excess of the 4 mm. to which the standard test is limited must be used, as the yield as a rule occurs at a higher penetration than 4 mm. For most practical instances 4 mm. lies below the yield point.

In view of this fact, care has been taken in the apparatus developed by the writer to provide for ample transport of the



standard plunger and for sufficient total weight to continue experiments as far as the yield point and beyond.

### The Gel Factor

The importance of a higher expression for gel strength was first suggested by Sheppard in terms of the torsional elasticity of the gel (9).

The slope of the load-versus-penetration characteristic alone, as indicated by one point on this slope (the Bloom figure) is not indicative alone of the gel strength of gelatin. What is indicative of gel strength is the total work necessary before the final break in the jelly occurs.

It is proper, therefore, to determine this gel factor in terms of the area of the triangle included between the load-versus-penetration curve and the abscissa. This total area  $OAB$  (Figure 6) is then

$$A = \frac{1}{2} \text{ the breaking load} \times \text{penetration (gram per cm.)}$$

In this specific instance the gel factor,  $J$ , would equal  $\frac{1}{2} \times 294 \times 0.75 = 110.6$  (gram per cm.). This result, multiplied by a numerical constant,  $C$ , can be compared with the expression for proof resiliency, as suggested by Sheppard in terms of the torsional elasticity of a standard jelly cast.

The term "gel factor" was suggested by the writer in 1935 in order to avoid confusion with the term "jelly strength" which in common use today is assumed to be proportionate to the Bloom number only (5).

For industrial control tests as well as for research work, it has been found more accurate to determine the value of

gelatin in terms of the gel factor. It is entirely possible to have a high gel factor despite a low Bloom number and vice versa. What seems to be most characteristic for gelatin is the amount of total work necessary before the final break in the jelly occurs, and not the amount of load to produce one haphazardly taken penetration depth. Tests should represent conditions that are actually of primary importance for the product, and not necessarily certain points that are convenient for a limited number of producers.

It is, of course, easily possible to attach a different plunger head of conical, needle-shaped, ball, or other desirable form. In this manner the apparatus lends itself also to penetrometer measurements, such as those described by Lutz, Culpepper, Moon, and Meyers (2).

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## Discontinuous Fractional Extraction Apparatus Utilizing Reflux

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Solvent-extraction processes are very useful in effecting the separation of complex liquid mixtures by physical means. This is especially true if reflux conditions and countercurrent contacting of the phases are employed. In this way, the sharpness of the separation is better and the segregation of the components more complete. This paper describes a suitable small-scale

batch-extraction process utilizing reflux for conditions where the solvent is either lighter or heavier than the liquid undergoing treatment.

The apparatus is shown to be reproducible, efficient, and practically self-operating. It permits the separation of a liquid mixture by solvents into as many fractions as desired.

FOR several years this laboratory has devoted some efforts to the development of the fundamentals of extraction, to the design of efficient extraction equipment, and to the application of these in the field of solvent refining of petroleum products (3, 5, 10-13).

This paper describes a discontinuous fractional extraction apparatus, developed in this laboratory, that is novel in design and satisfactory in operation. It is particularly valuable in the analysis of lubricating oils where a given batch of material must be resolved into its component parts. The results of such analyses will be given in subsequent papers.

### Principles of Design

Aside from auxiliary equipment for the control of temperatures and of rates of flow, the apparatus consists of three

main sections: a leaching section, a countercurrent contacting section, and a reflux-producing section.

The solvent is continuously introduced to the leaching section where the batch of oil to be solvent-fractionated is charged. There, a portion of the oil goes into solution, forming a solvent phase which separates because of density difference and flows into the contacting section. In general, the dissolved portion of the oil will contain the constituents of the charge in proportions that are in the order of their solubilities in the solvent and of their amounts in the charge. From the contacting section the solvent phase passes into a still where it is stripped of part or all the solvent. The resulting oil phase is returned to the contacting section where it flows countercurrent to the solvent phase; in this section the oil and solvent phases interact, with the result that the solvent phase becomes



richer while the oil phase becomes poorer in the more soluble constituents. The oil phase returns to the leaching section and mixes with the remainder of the charge ready for further leaching. The solvent phase proceeds to the still, is stripped of solvent, and the resulting oil phase is returned as reflux. The repetition of this operation concentrates the more soluble constituents of the charge in the reflux-producing section. This concentrate is then removed as product and the operation is repeated on the remainder of the charge, thus dividing it into as many portions as desired.

TABLE I. COMPARISON OF BATCH REFLUX EXTRACTIONS TO DETERMINE EFFECT OF AMOUNT OF CHARGE ON SHARPNESS OF SEPARATION

(Temperature of extraction = 77° F. (25° C.). Solvent (acetone) rate = 6.0 liters per hour.)

Property of Oil	—1-Gallon Charge— (4 Liters)			—5-Gallon Charge— (20 Liters)		
	Over-all oil	Extract	Raffinate	Over-all oil	Extract	Raffinate
Weight % of charge	100	15.2	82.6	100	17.2	81.1
Viscosity at 210° F. Centistokes	5.83	7.49	5.56	5.92	9.35	5.61
Saybolt seconds	44.5	49.7	43.7	44.8	56.1	43.8
Viscosity at 100° F. Centistokes	39.44	84.35	34.68	40.31	152.0	34.29
Saybolt seconds	183.7	389	161.9	187.7	702	160.2
Kinematic viscosity index	98	20	110	99	-27	115
Gravity, °A.P.I.	30.2	21.4	32.1	30.2	17.6	33.0
Specific gravity at 60° F.	0.875	0.925	0.865	0.875	0.949	0.860
Viscosity-gravity constant	0.820	0.875	0.809	0.820	0.900	0.804

LEACHING SECTION. The purpose of this section is to bring the solvent into intimate contact with the entire charge in order to produce continuously differential amounts of solvent phase in substantial equilibrium with the oil phase. This may be approached in practice by forcing the solvent into the charge of oil through spray nozzles that atomize the solvent, and by otherwise keeping the charge reasonably well agitated.

In addition to providing intimate solvent-oil contact and proper mixing, the leaching section for batch operation must be large enough so that the holdup of oil in the column may be small compared with the charge. Keeping other variables constant, the effect of the amount of charge is shown in Table I. Sharpness of separation increased appreciably when a 5-gallon (20-liter) replaced a 1-gallon (4-liter) charge. On the average, 16 per cent separation yielded an extract with a viscosity of 702 Saybolt seconds at 100° F. (37.8° C.) and a viscosity index of -27 in the case of the 5-gallon charge, as against an extract of 389 Saybolt seconds at 100° F. and a viscosity index of +20 in the case of the 1-gallon charge. In this and the following tables the original oil had substantially the properties as given in Table IV—i. e., it was a neutral oil of about 100 viscosity index.

In all this work viscosities were determined in modified Ostwald viscometers (2, 4) and conversion from kinematic viscosity to Saybolt seconds and calculation of kinematic viscosity indexes were made from experimental relations (6, 8). Gravities were determined with hydrometers (1) and the viscosity-gravity constant was calculated by the method of Hill and Coats (7).

COUNTERCURRENT CONTACTING SECTION. Even in the ideal case where the solvent differentially dissolves out of the charge portions of oil in equilibrium concentrations, the sol-

vent phase will still contain appreciable amounts of the less soluble constituents. It is therefore desirable to separate the latter and to replace them with the more soluble constituents. This is the function of the countercurrent contacting section. In this section the oil phase formed in the reflux-producing section and the solvent phase formed in the leaching section flow countercurrently. In a properly designed column, at each cross section the oil phase comes in contact with a solvent phase that is poorer in the more soluble constituents than required by the equilibrium relations. This induces interaction between the phases, with the result that the ratio of the more soluble constituents to that of the less soluble constituents increases in the solvent phase and decreases in the oil phase.

Other factors being the same, the extent of interaction will depend on the interfacial area between the two phases. In order to increase this area as much as practicable, various means may be employed. Of these, the use of spray nozzle or of packing to divide the refluxed oil into small globules is the more common. In batch extraction, where both the viscosity and the amount of refluxed oil vary with time, the use of packing is simpler. It has an additional advantage over the use of spray nozzles in that if there is any tendency for the oil globules to coalesce, the packing tends to divide them again. The advantages of using a packing material in the extraction tower, also when the oil formed the continuous phase, were shown by Rushton (9).

Table II presents data showing the effect of various packings on the quality of approximately 15 per cent extract from a given oil. Of the packings investigated, 0.25-inch carbon rings gave the better results, yielding an extract with a viscosity of 407 Saybolt seconds at 100° F. (37.8° C.) and a viscosity index of 19, while No. 15 iron jack-chain or a 3.00 Monarch spray nozzle gave less efficient results, yielding an extract with a viscosity of around 340 Saybolt seconds at 100° F. and a viscosity index of 33. The differences, however, are small, and the advantage to be gained by using one packing instead of another is slight as compared with the effect of other factors, such as the amount of charge (see Table I).

It should be noted that the per cent of the charge held up in the contacting section may be different for different packings, and therefore in batch runs the effect of holdup will be combined with those of the other characteristics of the packing, such as shape, size, etc. Semicontinuous runs where, after steady conditions are established, the extract and raffinate are removed and replaced with another batch of the same quality charge without removing the holdup in the system, and this process is repeated until the successive extracts and raffinates do not change in composition and amount and add up to those of the charge, may be used instead. Experiments using a 1-gallon (4-liter) charge show that this condition is approached after three successive batch runs. Table III gives data obtained in this manner. It is evident that, although the

TABLE II. COMPARISON OF BATCH REFLUX EXTRACTIONS TO DETERMINE EFFECT OF TYPE OF PACKING ON SHARPNESS OF SEPARATION

[Solvent = acetone. Temperature of extraction = 77° F. (25° C.). Charge = 1 gallon (4 liters).]

Property of Oil	Packing					
	1/4-inch carbon rings	1/4-inch glass rings	3/8-inch porcelain rings	1/2-inch carbon rings	None, 3.00 Monarch spray nozzle	No. 15 iron jack-chain
Extract, weight % of charge	14.7	14.6	13.9	13.6	15.1	14.7
Viscosity at 210° F.: Centistokes	7.62	7.48	7.37	7.21	7.16	7.14
Saybolt seconds	50.1	49.7	49.3	48.8	48.6	48.6
Viscosity at 100° F.: Centistokes	88.4	84.5	80.8	76.0	74.2	73.5
Saybolt seconds	407	389	373	350	342	339
Kinematic viscosity index	19	20	24	30	33	34
Holdup, weight % of charge	37	16	17	21	15	22
Solvent rate, liters per hour	9.9	6.5	6.5	7.4	10.4	6.6



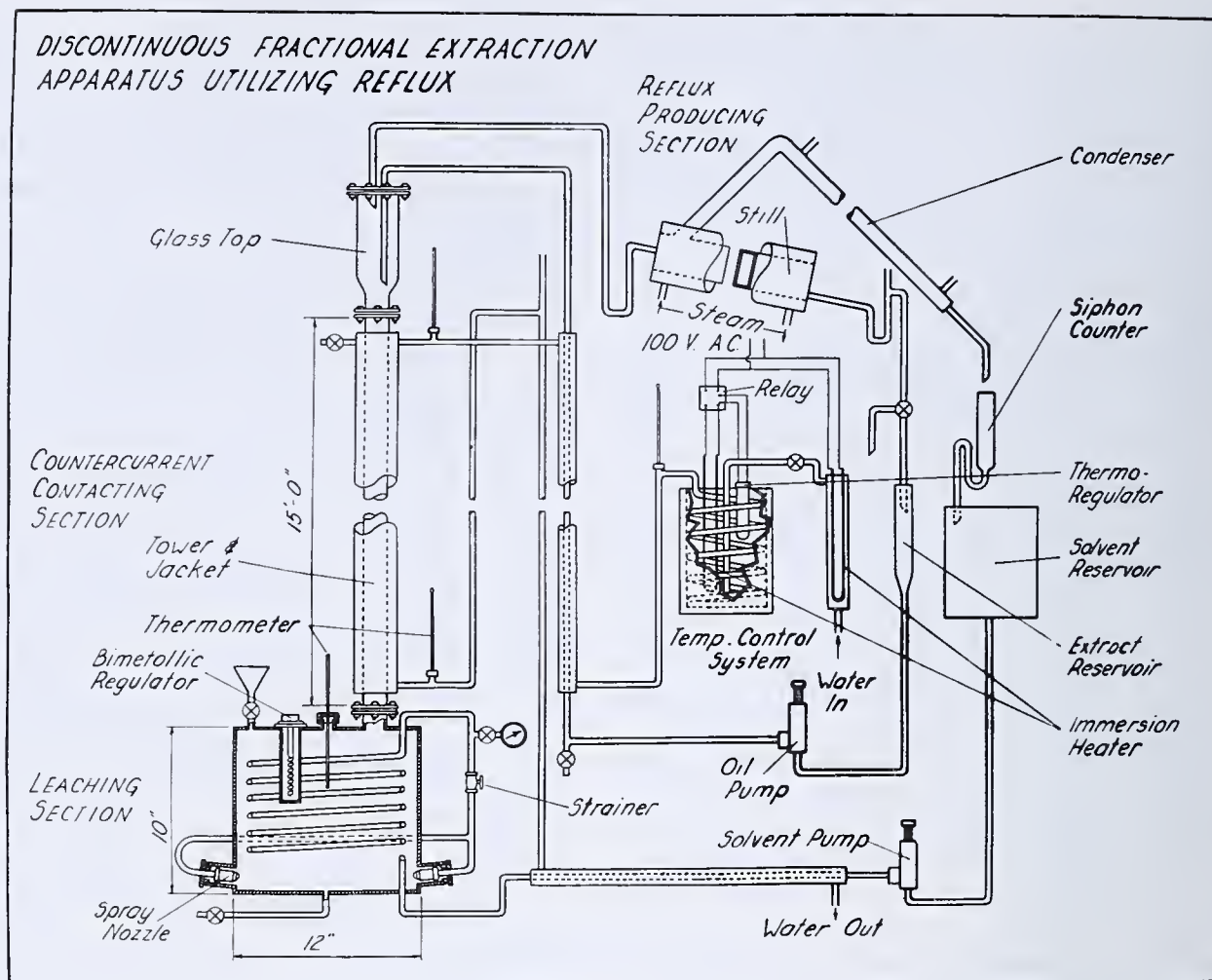


FIGURE 1

packings are in general rated as in the batch runs, reversals in rating are also found. These are believed to be due to the disappearance of the holdup effect and to the difficulty of getting strictly steady conditions. A point that is significant in connection with the semicontinuous runs is that better separation is obtained when compared with the batch runs, using the same packing and extracting the same percentage from a given oil. Thus, using 0.25-inch carbon ring packing and extracting approximately 15 per cent, the semicontinuous method gave an extract of 584 Saybolt seconds at 100° F. (37.8° C.) and a viscosity index of -18, compared with an extract of 407 Saybolt seconds at 100° F. and a viscosity index of +19 obtained when using the batch method.

Finally, for a given per cent extract, higher viscosity and lower viscosity index may not always mean sharper separation even though the solvent and charging stock used are identical. However, with the particular solvent-oil system and

the per cent extraction employed in these experiments, such an assumption is well justified.

TABLE IV. PROPERTIES OF OIL USED IN PACKING INVESTIGATION

Gravity, °A. P. I.	30.8
Specific gravity at 60° F.	0.872
Viscosity at 100° F.:	
Centistokes	38.55
Saybolt seconds	179.6
Viscosity at 210° F.:	
Centistokes	5.80
Saybolt seconds	44.4
Flash point, ° F.	425 (218° C.)
Fire point, ° F.	490 (254° C.)
Pour point, ° F.	+25 (-4° C.)
Color, A. S. T. M.	4
Conradson carbon residue, per cent	0.01
Kinematic viscosity index	101

Table IV gives inspection data on the oil used in all the experiments on investigating the effect of packing.

TABLE III. COMPARISON OF SEMICONTINUOUS REFLUX EXTRACTIONS TO DETERMINE EFFECT OF TYPE OF PACKING ON SHARPNESS OF SEPARATION

[Solvent = acetone. Temperature of extraction = 77° F. (25° C.). Charge = 1 gallon (4 liters). Number of charges = 3.]

Property of Oil	Packing					
	1/4-inch carbon rings	1/2-inch carbon rings	3/8-inch porcelain rings	None, 3.00 Monarch spray-nozzle	1/4-inch glass rings	No. 15 iron jack-chain
Extract, weight % of charge	15.5	15.1	14.3	15.7	15.0	15.0
Viscosity at 210° F.:						
Centistokes	8.64	8.53	8.44	8.25	8.26	8.10
Saybolt seconds	53.6	53.3	52.9	52.2	52.2	51.7
Viscosity at 100° F.:						
Centistokes	126.7	123.7	118.2	111.6	109.2	106.0
Saybolt seconds	584	571	546	514	503	489
Kinematic viscosity index	-18	-18	-11	-7	-1	-2
Solvent rate, liters per hour	6.5	7.5	6.4	6.5	6.5	6.6

**REFLUX-PRODUCING SECTION.** Here, the solvent phase leaving the counter-current contacting section is stripped of its solvent to produce an oil phase. The solvent is returned to the leaching section while the oil phase flows to the contacting section. Other means of producing reflux, such as cooling or adding precipitating agents, etc., may be used, if desired, in place of distillation. Vacuum or pressure may be applied to the system to keep within the desired temperature range, depending on the solvent employed.

Varteressian and Fenske (12) have outlined the factors that must in



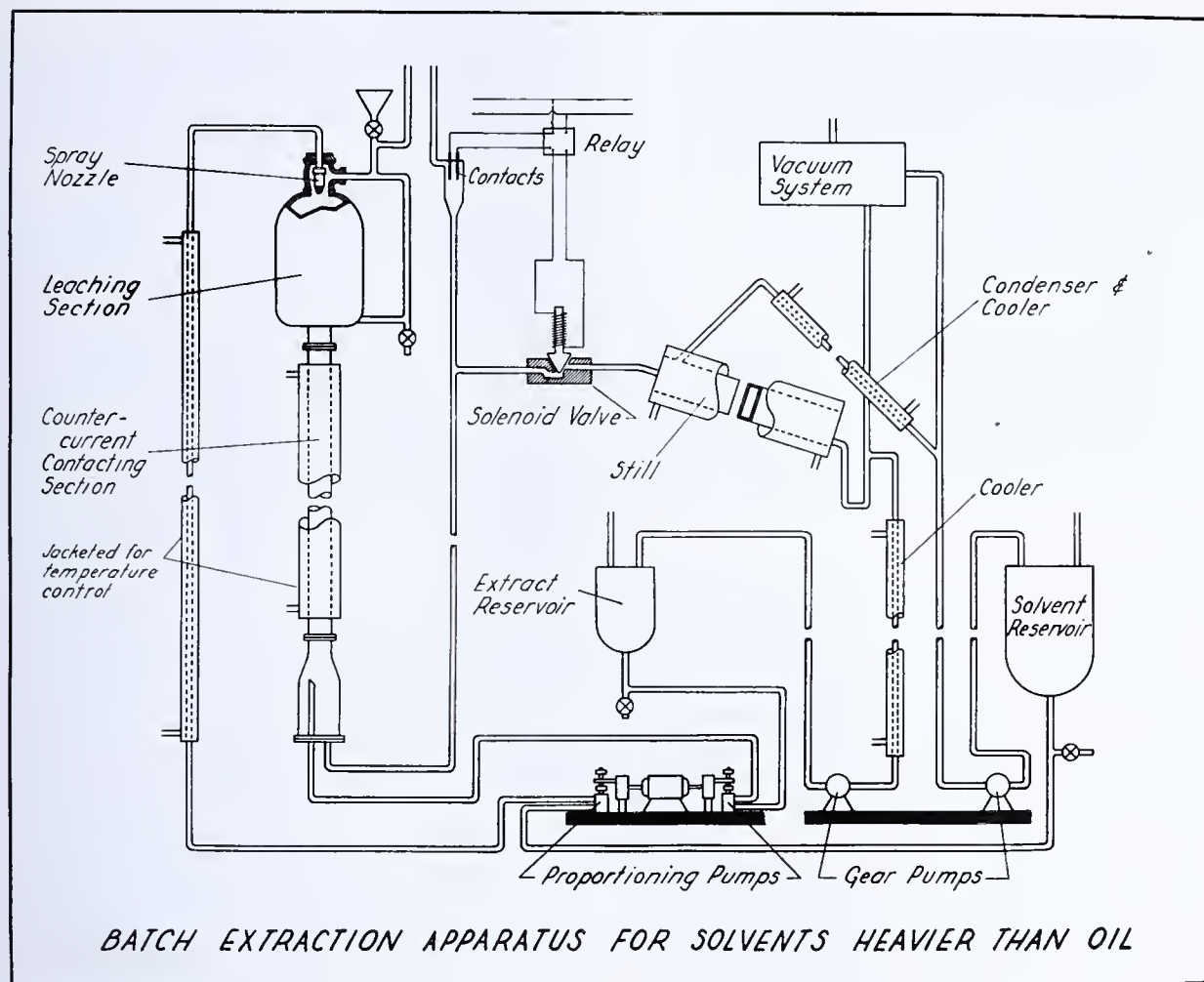


FIGURE 2

General be considered for the proper use of reflux. Ordinarily, when the refluxed oil phase meets the solvent phase in the contacting section, two processes take place: (1) the solvent phase dissolves the more soluble constituents of the refluxed oil; (2) the less soluble constituents of the oil in the solvent phase are precipitated. With lubricating oils, the constituents of which differ considerably from each other in solubility, the first of the above processes may become predominating.

A third process that may take place, especially with oil charges of high aromatic content, is that the refluxed oil phase entirely dissolves in the solvent phase. The solution thus formed, being different in density from the solvent phase in the contacting section, tends to flow countercurrent to it. When it reaches a region in the contacting section where the contents of the saturated solvent phase are more paraffinic, the two solutions of different densities interact and precipitate small globules of a paraffinic oil phase. In one instance, using a 10-foot (3-meter) glass column, and an oil charge having a viscosity index of 14 and a 100° F. (37.8° C.) viscosity of 468.5 Saybolt seconds, a reflux oil phase was first observed in the column at a point 3.5 feet (107 cm.) from the point of introduction of reflux. Under such conditions of extraction, the 16 per cent extract had a viscosity index of -79 and the 48 per cent raffinate a viscosity index of 10. The remainder of the charge (36 per cent) was held up in the column; its viscosity index was -48. The solvent used was acetone at 20° C. The

100° F. (37.8° C.) viscosities of the extract, raffinate, and holdup were 1136, 187.4, and 925 Saybolt seconds, respectively. It is obvious that good separation was obtained.

In order to establish definitely the effect of reflux on the nature of separation, an oil was fractionally extracted into approximately 5 per cent cuts under identical conditions with and without the use of reflux. A detailed discussion of the results obtained with such procedures will be presented later. Table V, however, is included here, to show the differences in the cuts obtained at various stages of the extraction, both with and without reflux. The procedure described with the heading "no reflux" is analogous to simple distillation, while "reflux" signifies a procedure analogous to fractional distillation under total reflux, in both cases the solvent, acetone, taking the place of heat.

The superiority of separation when utilizing reflux is striking. For instance, when cut A is compared with cut B, it is obvious that during the first stages of extraction reflux has very

TABLE V. COMPARISON OF BATCH EXTRACTIONS, WITH AND WITHOUT REFLUX, TO DETERMINE EFFECT OF REFLUX ON SHARPNESS OF SEPARATION

[Temperature of extraction = 77° F. (25° C.). Charge = 5 gallons (20 liters). Solvent (acetone) rate = 5.5 liters per hour (0 to 20% extracted); 10.0 liters per hour (20 to 100% extracted).]

Property of Oil	Over-All Oil	Cut A, 0 to 5%, Approximate		Cut B, 40 to 45%, Approximate		Cut C, 90 to 100%, Approximate	
		Reflux	No reflux	Reflux	No reflux	Reflux	No reflux
Viscosity at 210° F.: Centistokes	5.93	8.84	7.09	4.78	5.51	8.29	7.33
Saybolt seconds	44.8	54.3	48.4	41.3	43.5	52.4	49.2
Viscosity at 100° F.: Centistokes	39.86	142.2	64.78	27.08	35.47	56.48	47.94
Saybolt seconds	185.6	656.0	299.4	128.1	165.4	261.0	222.0
Kinematic viscosity index	101	-37	+60	+115	+102	+124	+123
Gravity, ° A. P. I.	30.2	16.0	23.3	32.9	30.9	33.8	34.1
Specific gravity at 60° F.	0.8751	0.9593	0.9141	0.8607	0.8713	0.8560	0.8545
Viscosity-gravity constant	0.820	0.915	0.863	0.809	0.817	0.790	0.790



appreciably aided in the separation of the highly viscous components of low viscosity index from those having lower viscosities and higher viscosity indexes, whereas straight extraction has only partially succeeded in doing so. Again, comparing cut *B* with cut *C*, it is noticed that during the last stages of extraction, reflux has made possible a better separation of the more viscous from the less viscous of the high viscosity index constituents, than has straight extraction.

### Apparatus and Procedure

Figures 1 and 2 present discontinuous fractional extraction equipments using solvents lighter and heavier, respectively, than the charging stock. Only the unit in Figure 1, for the lighter solvents, will be discussed in detail because it was the one used in obtaining the results reported here. The design and operation of the unit for heavier solvents will then be obvious.

The leaching section consists of a cylindrical steel container 1 foot (30.5 cm.) in diameter and 10 inches (25.4 cm.) high, with a capacity of approximately 5 gallons (20 liters), with provisions for introducing and withdrawing its contents. Two openings are provided at the lower end of the container where spray nozzles (No. 3, Type F-27, purchased from the Monarch Manufacturing Works, Inc., Philadelphia, Pa.) for introducing the solvent are fitted at such angles to each other as to tend to give the contents of the container a slight rotary or swirling motion. The solvent, before reaching the nozzles, is pumped through a steel coil located inside the leaching section for the purpose of ensuring a temperature substantially the same as that of the oil charge. A pressure gage and a strainer are inserted in the line. The leaching drum is heated electrically to the desired constant temperature by means of resistance wire wound around it and a bimetallic regulator-relay system. A thermometer is inserted directly inside the drum.

The countercurrent contacting section consists of a 15-foot (4.6-meter) length of No. 16 B. & S. gage seamless steel pipe 2 inches (5 cm.) in outside diameter, having a capacity of 2.14 gallons (8.10 liters). Two small lugs, brazed on the inside of the pipe at the bottom of the tower hold a ring having several cross wires to support the packing material in the column. In order to maintain the desired temperature in the tower, the latter is jacketed with a seamless steel pipe 3 inches (7.5 cm.) in outside diameter, for circulating water in the annular space. It will be noticed that provision is made, through proper piping, to introduce the water at the top end of the tower, so that countercurrent cooling is possible for extraction using a temperature gradient in the contacting section. Thermometers are inserted at the entrance and exit of water to the jacket.

A specially fabricated Pyrex glass top permits detection of entrainment of oil in the upward-flowing solvent phase. It is 1 foot (30.5 cm.) long and 3 inches (7.5 cm.) in diameter except at the bottom for a length of about 3 inches (7.5 cm.), where it is reduced to a 2-inch (5-cm.) diameter and flanged to the 2-inch tower. The top of the glass pipe is closed with a steel plate fastened with a flange. This plate contains an overflow line leading to the still for stripping the solvent, and a second line for introducing reflux, centered within the glass pipe, the tip of which extends to within 2 inches (5 cm.) of the bottom of the glass section.

The constant-temperature water supplied to the tower jacket, as well as to the solvent and reflux oil inlet jackets, is obtained by running tap water through a copper coil inserted in a water bath. Electric immersion heaters and a mercury regulator-relay system give satisfactory control of temperature.

The reflux-producing section consists of a still made of a 3-foot (91.5-cm.) length of square Shelby steel tube, 3 inches (7.5 cm.) in outside diameter, jacketed with a 5-inch (12.5-cm.) standard steel pipe, with suitable openings for introducing steam into the annular space. The still is inclined, and an inlet is provided at the upper end and an outlet for the nonvolatile liquid at the lower end; both inlet and outlet lines have traps to prevent the escape of vapors. The vapor line is a 1.5-inch standard steel pipe, brazed to the 3-inch tube at an angle, and leads directly to a condenser which consists merely of a continuation of the vapor line set at a right angle and containing a coil of 0.3125-inch (8-mm.) copper tubing through which the cooling water flows. A siphon-counter, placed beneath the discharge end of the condenser, permits measurement of the condensate rate of flow into the solvent reservoir. The oil line from the still leads into a graduated extract reservoir. Both reservoirs are directly connected each to a piston-type Hills-McCanna proportioning pump driven by a Janette  $1\frac{1}{2}$  h. p., 1750 r. p. m., motor and speed reducer having a 56 to 1 gear ratio. The extract reservoir contains a level-control device (not shown in drawing) which enables the pump to adjust its stroke automatically according to the rate at which the oil flows into the reservoir from the still, so that a constant, predetermined amount of oil is held in the reservoir and reflux is adjusted according to the solubility of the cut.

The unit is very simple to operate. The oil to be solvent fractionated is charged in the leaching section and the solvent in the solvent reservoir. After adjusting water rates and temperatures, the solvent pump is started at the desired rate, and the level control in the extract reservoir is set to give the desired amount of extract cut. After the solvent phase reaches the top of the tower, it overflows into the still. The solvent from the still flows to the solvent reservoir, while the oil phase accumulates in the extract reservoir. As this oil phase reaches a predetermined volume (say, 5 per cent of the charge) the oil pump is allowed to send reflux to the top of the tower at a rate equal to the inflow of oil phase to the reservoir. This operation is simply continued until steady conditions of extract rate and quality are obtained. The time required for the establishment of steady conditions will depend on the rate of throughput, the per cent extracted, the packing employed, the temperature of extraction, and the oil and solvent used. When steady conditions are established, the extract reservoir is emptied and another cut is obtained in a similar manner. This is repeated until a desired percentage of the charge is divided into the desired number of extraction cuts.

At the completion of the run the contents of the leaching section and the countercurrent contacting section are pumped to the still through a line in the bottom of the leaching section. Solvent is then recirculated through the apparatus until the last traces of oil have been washed from the packing and lines. The apparatus is finally drained in preparation for another run.

In order to follow the course of extraction and to find the time at which steady conditions have been established, it is desirable to follow some property of the oil, the measurement of which is simple and does not require a large sample. Refractive index is found satisfactory for this purpose. Table VI presents data on the variation with time of the refractive index of the oil from the still. It is evident that, under the conditions of the experiment somewhere between 2 and 3 hours from the time reflux occurred, steady conditions were established.

It is of course to be granted that two samples of a complex solution (such as a lubricating oil cut) that have a single property (such as refractive index) in common may not necessarily be identical in other properties. However, using a given oil and a given solvent, and extracting out a given percentage, the

TABLE VI. VARIATION OF REFRACTIVE INDEX OF REFLUX OIL WITH TIME

[Temperature of extraction = 77° F. (25° C.). Charge = 1 gallon (4 liters). Solvent (acetone) rate = 5.5 liters per hour. Weight per cent extracted = 2.]

Elapsed Time <sup>a</sup>	Oil Rate from Still	Refractive Index of Reflux, $n_D^{20}$	Total Solvent Used
Hours	Cc./hour		Liters
0.67	360	1.5143	11.4
0.67	456	1.5150	16.8
1.67	582	1.5199	22.2
2.67	870	1.5230	27.6
3.67	925	1.5230	33.0
4.67	948	1.5231	38.4

<sup>a</sup> Measured from time reflux occurred.

TABLE VII. VARIATION OF REFRACTIVE INDEX OF REFLUX OIL WITH OTHER PROPERTIES

[Temperature of extraction = 77° F. (25° C.). Charge = 1 gallon (4 liters). Solvent (acetone) rate = 5.5 liters per hour.]

Run No.	Time of Run Hours	Weight Per Cent	Refractive Index, $n_D^{20}$	Viscosity at 100° F. Saybolt Sec.	Viscosity Index
4	1	1.97	1.5151	348	33
7	3	2.02	1.5215	418	11
6	5	2.10	1.5230	476	-1
5	8	2.07	1.5226	467	1



establishment of any one property of the cut usually defines, within a narrow range, the rest of the properties at least for practical purposes. The data in Table VII, for instance, show that as the refractive index of the extract becomes constant, so do also its viscosities and viscosity indexes. They represent different runs of different durations, and not only show that there is no need to carry on the run beyond at most 5 hours, but also that by simply following the refractive index of the reflux oil it is possible to predict the constancy of quality of the extract.

### Acknowledgment

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## Fused Magnesia Crucibles

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**N**O MATTER is of greater importance nor of more concern to the metallurgist and to the operator of a high-temperature furnace than the kind, life, and use of the refractory that forms the melting chamber.

### Melting Point

The melting point of a refractory material does not determine the temperature to which a charge in the crucible may be safely heated. The manner of heating is very important. Kanolt (6) states that magnesium oxide heated under reduced pressure (0.5 to 1.0 cm. of mercury) volatilizes completely before it melts. When heated at atmospheric pressure in contact with carbon, magnesium oxide volatilizes rapidly at temperatures above 2000° C. If the metal within the crucible is heated directly by induction in the high-frequency induction furnace the metal is always hotter than the crucible, whereas if the metal is heated indirectly by conduction of the heat through the wall of the crucible the crucible is always as hot as, if not hotter than, the metal within it. Small amounts of impurities such as bonding materials used in forming the crucibles may lower the softening point of the crucibles by several hundred degrees below the melting point of the pure refractory material. Roller and Rittenberg (8) found that fused magnesia crucibles fired to approximately 1600° C. in a high-frequency induction furnace sometimes melted at the base. They state: "This illustrates that there is a region of crucible flow at high temperatures rather than a sudden melting down."

### Reactions of Fused Magnesia with Carbon

Swanger and Caldwell (12) suggest that graphite molds be used in forming the crucibles, since magnesium oxide does not form carbides and the crucibles can be heated to 1800° C. in the molds in which they were formed. Kanolt (6) found that magnesium oxide when heated at atmospheric pressure in contact with carbon volatilized rapidly at temperatures above 2000° C. Roller and Rittenberg (8) reported that

dense fumes were evolved when magnesium oxide was heated in contact with carbon at temperatures of about 2500° C.

### Methods of Making Small Crucibles

Processes for the manufacture of magnesia crucibles have been described by Burgess and Aston (1), Cain, Schramm, and Cleaves (2), Yensen (14), Fergerson (3), and Watts (13). Mehl (7) states: "In all of these processes the purified magnesium oxide was first shrunk by heating to a temperature near 1600° C., then ground and pressed into a mold under high pressure, and finally heated to a temperature at which sintering occurs, with consequent cohesion of the rather coarse particles of magnesium oxide."

Mehl mixed a thick sirup of shellac in absolute alcohol with the calcined c. p. magnesia and packed the mixture into a brass mold. The core and then the base were removed, and the crucible was dried for several hours in a brisk current of air. The crucible was then removed from the mold and dried for several hours in an air oven at 100° to 130° C. The dried crucible was fired in an electric furnace.

Jordan, Patterson, and Phelps (5) found that commercial fused magnesium oxide was not pure enough for preparing crucibles for use in melting pure metals. Since the chemical reagent grade of unfused magnesium oxide shrinks a great deal when heated to 1600° C. it is necessary to calcine it before using it to form crucibles. They moistened <100-mesh calcined oxide with a 2 per cent solution of  $MgCl_2 \cdot 6H_2O$ , tamped the mixture into a graphite mold, and fired in the mold at 1600° to 1800° C. The crucibles were very hard and dense and had an almost porcelainlike body or texture. The apparent specific gravity of such crucibles was about 3.5. They found that the addition of about 15 per cent of a mixture of equal parts of 100- and 200-mesh purified white zirconium silicate increased the strength of magnesia crucibles. Zirconium silicate often contains phosphorus.

Schuette (10) tamped <60-mesh periclase, a commercial fused-magnesia electric-furnace product containing 95.1 per cent  $MgO$ , into graphite molds. No binder was used. The crucibles were fired in the molds at about 2500° C. in a high-frequency induction furnace. Shrinkages of 0.317 cm. (0.125 inch) in a 6.35-cm. (2.5-inch) crucible were observed.

Swanger and Caldwell (12) moistened <60-mesh electrically fused magnesium oxide with a water solution of  $MgCl_2 \cdot 6H_2O$



(2 per cent by weight of the magnesium oxide needed for the crucible in a minimum amount of water). They used a chisel-pointed tool for tamping the moistened refractory into the mold to eliminate "rings" marking the successive additions of refractory material.

Salmang and Planz (9) prepared highly refractory dense crucibles by using mixtures of different-sized particles of magnesia. The best mixture they used consisted of 10 per cent <65 >200-mesh calcined magnesia, 80 per cent <200-mesh calcined magnesia, and 10 per cent <200-mesh unburned magnesia. The mixture was moistened with 10 per cent of its weight of magnesium chloride solution (30 per cent  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). After drying, the crucibles were burned at  $2000^\circ\text{C}$ .

Herty (4) made very satisfactory crucibles from <100-mesh fused magnesia mixed with sufficient 1 to 1 hydrochloric acid so that it could be molded readily. The mixture was put into an iron mold under slight pressure. The crucible was removed, dried at  $110^\circ\text{C}$ ., and then burned at  $1600^\circ\text{C}$ . for 3 hours.

Roller and Rittenberg (8) prepared impervious crucibles, about 3.53 cm. (1.39 inches) in internal diameter, 4.98 cm. (1.96 inches) high, with 0.3-cm. (0.12-inch) wall thickness from carefully sized magnesium oxide particles. The refractory powder was moistened with about 10 per cent of its weight of water that was approximately 0.25 *M* in hydrochloric acid and 0.25 *M* in *o*-phosphoric acid. The moistened powder was pressed in two steps to ensure uniform density and strength. Pressures up to 40,000 pounds per square inch on the wall and 15,000 pounds per square inch on the base were used. The crucibles were air-dried for 24 hours and then dried at  $120^\circ\text{C}$ . for several hours. The dried crucibles were fired in a high-frequency induction furnace to a maximum temperature of  $2600^\circ\text{C}$ .

Siegel (11) recommends that fused magnesia bonded with 3 per cent slaked lime and 0.5 per cent fireclay be used in the manufacture of slagproof crucibles for the coreless induction furnace.

### Resistance to High Temperatures and Chemical Reactions

Kanolt (6) states that magnesia crucibles have been used at  $1800^\circ\text{C}$ . If not in contact with carbon, such crucibles probably could be used at temperatures several hundred degrees higher.

TABLE I. COMPOSITIONS OF SLAGS USED IN TESTING CRUCIBLES

Slag No.	CaO %	MgO %	FeO %	Fe <sub>2</sub> O <sub>3</sub> %	MnO %	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	P <sub>2</sub> O <sub>5</sub> %
1					76.3	23.7		
2	42.5	7.6	9.4	4.1	12.8	20.8	1.5	1.6
3	48.0	5.7	12.4	5.4	6.3	4.7	0.6	17.5

Salmang and Planz (9) tested their crucibles by heating in contact with (1) a basic manganese silicate slag, (2) a Siemens-Martin slag, and (3) a Thomas slag at temperatures of  $1470^\circ$  to  $1600^\circ\text{C}$ . The compositions of the slags are shown in Table I.

During melting the magnesia content of the slags increased (1) in the basic manganese slag from 0.0 to 3.7 per cent, (2) in the Siemens-Martin slag from 7.6 to 8.4 per cent, and (3) in the Thomas slag from 5.7 to 5.9 per cent.

TABLE II. SOLUTION OF MAGNESIA BY MOLTEN  $\text{CaO-MgO-FeO-SiO}_2$  SLAG HELD IN A FUSED MAGNESIA CRUCIBLE

Time of Contact Min.	Magnesia in Slag %
0	3.88
5	5.36
10	6.71
15	10.21

Salmang and Planz (9) reported that the thermal expansion of their crucibles was so small that the crucibles could be quenched in water from  $1600^\circ\text{C}$ . without cracking.

Tests (8) in Roller and Rittenberg's impervious magnesia crucibles showed that molten ferrous oxide could be held in them for some time. A slag consisting of 70 per cent FeO and 30 per cent  $\text{SiO}_2$  was held at  $1525^\circ \pm 25^\circ\text{C}$ . for 20 minutes

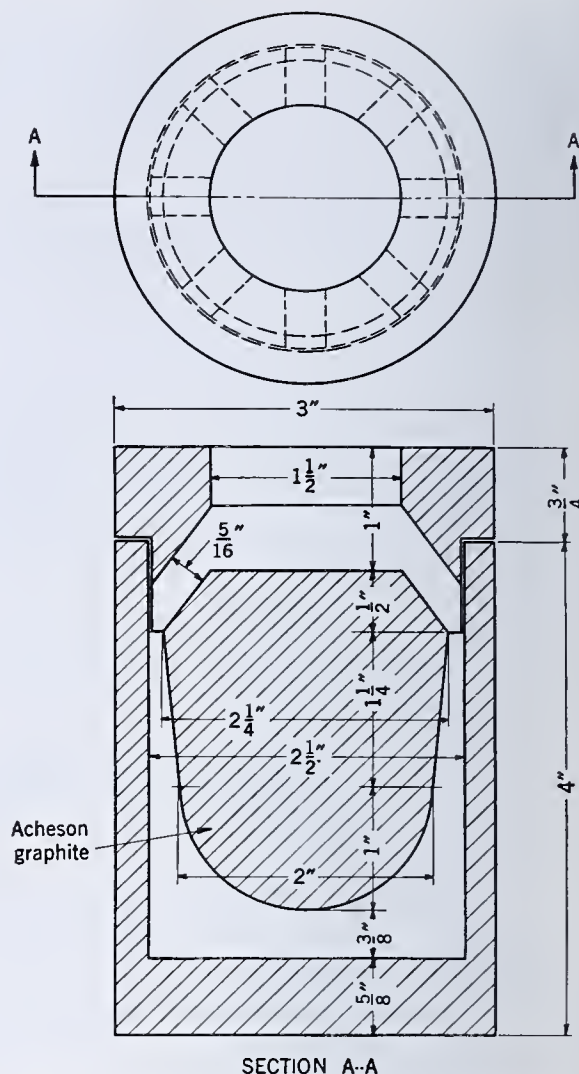


FIGURE 1. GRAPHITE MOLD FOR FORMING CRUCIBLES

without much damage to the crucible. Tests by Herty (4) at the Bureau of Mines, Pittsburgh, Pa., showed that at high temperatures a molten slag containing 50 per cent CaO, 3 per cent FeO, and 15 per cent  $\text{SiO}_2$  did not penetrate the crucibles over "a considerable period of time," whereas in dense but porous magnesia crucible the slag penetrated the crucible as rapidly as the slag melted. Although the molten slag was retained by the impervious magnesia crucible, chemical action occurred as shown in Table II.

### Improved Method

In the improved method dry refractory material is packed in specially designed molds by means of an electric vibrator.

A diagrammatic sketch of one of the molds is shown in Figure 1. The core, A, and the crucible were machined from Acheson graphite electrodes. A photograph of three cores of different sizes together with magnesia crucibles formed around them is shown in Figure 2.

The dry refractory materials were of mixed sizes to provide a dense packing mixture. Crucibles were formed from two lots of electrically fused magnesia. The screen sizes of the materials are shown in Table III.

TABLE III. SCREEN SIZES OF FUSED MAGNESIA USED IN FORMING CRUCIBLES

Screen Size	Lot 1 Cumulative		Lot 2 Cumulative	
	%	%	%	%
>65-mesh	0	0	15.4	15.4
<65- >100-mesh	0.5	0.5	26.6	42.0
<100- >200-mesh	47.1	47.6	26.0	68.0
<200-mesh	52.4	100.0	32.0	100.0



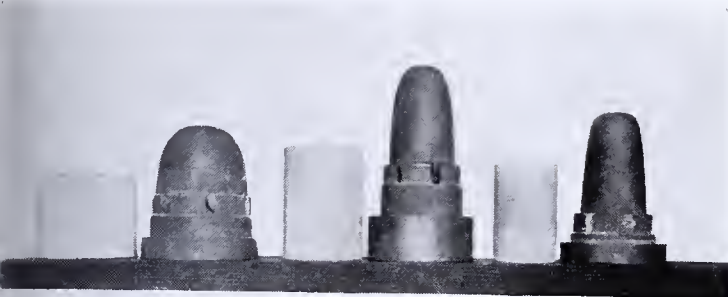


FIGURE 2. VARIOUS SHAPES AND SIZES OF CRUCIBLES AND CORES

The dry refractory material was poured into the depression in the upper portion of the core, A, Figure 1, while the entire mold was held on a 110-volt, 2-ampere electric vibrator as shown in Figure 3. The maximum packing was obtained by subjecting the filled molds to vibrations for 25 to 30 seconds. The volume of the dry refractory material poured into a graduated cylinder decreased 22 per cent when the filled cylinder was subjected to vibrations for 25 to 30 seconds.

The material in the depression in the core was poured out and the depression was filled with water. Experiments showed that the absorption of about 15 per cent by weight of water by the packed dry refractory material aided in the removal of the core and produced a smoother surface on the interior of the crucible. After the core had been removed the graphite crucible was heated on a hot plate or over a burner until dry. The use of water containing 1.5 to 3 per cent of boric acid decreases the temperature at which the refractory material must be heated to form a strong bond between the grains.

### Firing the Crucibles

The graphite crucible containing the dried refractory lining was heated in a high-frequency induction furnace to 1650° to 1700° C. in about an hour. When the furnace had cooled to about 800° C. the graphite crucible containing the refractory lining was removed and allowed to cool to room temperature. In order to prevent burning of the upper portion of the graphite mold a graphite cover was placed upon it. The mold was covered while being heated and until cooled to low red heat.



FIGURE 3. FILLING A MOLD HELD ON AN ELECTRIC VIBRATOR

### Shrinkage during Firing

Shrinkage of about 0.31 cm. (0.125 inch) in diameter was observed after firing magnesia crucibles 6.35 cm. (2.5 inches) in diameter when formed. Because of the shrinkage the crucibles after firing were easily removed from the graphite molds in which they were formed. This made possible the re-use of the molds for forming additional crucibles. An operator using 3 molds and 1 core can keep a high-frequency induction furnace in almost continuous operation firing refractory crucibles.

### Service Tests of Vibrator-Packed Crucibles

A large number of crucibles 6.35 cm. (2.5 inches) in diameter by 6.35 cm. (2.5 inches) high, having a projection 1.27 cm. (0.5 inch) in diameter by 0.635 cm. (0.25 inch) long at the center of the bottom, were prepared from lot 1 fused magnesia.

When the loose refractory material had been poured out of the depression into the graphite core, 15 per cent, by weight, of water containing 3 per cent boric acid was added. When the solution was absorbed the core was removed and the crucible dried on a hot plate. The dried crucible was heated in a high-frequency induction furnace to about 1650° C. in about an hour. Heating to a higher temperature for a longer time probably would have produced a better crucible. This was not tried since the crucibles withstood the service to which they were put.

The crucible was placed on the upper end of a rotatable spindle in a high-frequency induction furnace. The projection on the bottom of the crucible fitted into a 1.27-cm. (0.5-inch) hole at the center of the top of the spindle. About 200 grams of Armco iron were placed in the crucible. When the iron was melted the crucible was rotated at 280 r. p. m. Starting, stopping, and continuous rotating at 1550° to 1600° C. for several hours did not damage the crucible.

### Advantages of Improved Method

The crucibles are easily and rapidly formed. It is not necessary to use binders. The molds are easily machined. The crucibles are fired in the molds in which they are formed. The shape of the crucibles may be readily controlled. The crucibles have dense uniform structure. The molds and refractory may be dried rapidly and placed in a red hot furnace without injury to the refractory lining. The molds and crucibles may be removed from a red-hot furnace without damaging the refractory crucible.

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# A Complete Mercury- Purification System

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IN VARIOUS recommended laboratory methods of purifying mercury some or all of the following unit operations are used: washing and drying, oxidation of impurities by aeration, distillation, and electrolysis.

The method of Meyer, 1863 (7), of washing by passing the mercury in a fine stream through a long column of dilute nitric acid is well known. Better washing through a given height of column is obtained by using the "zigzag" column of Friedrichs (4). Drying has usually been done in an open dish. Alewijn (1) and Burstyn (3) passed air through mercury as a separate operation to remove some of the metallic impurities as oxides, following this step by filtration. More often air is bubbled through the mercury during distillation as described by Hulett (6). A number of papers have been published describing glass or metal stills, some automatic, operating under various degrees of reduced pressure. There are several descriptions of electrolytic methods (2, 5, 8).

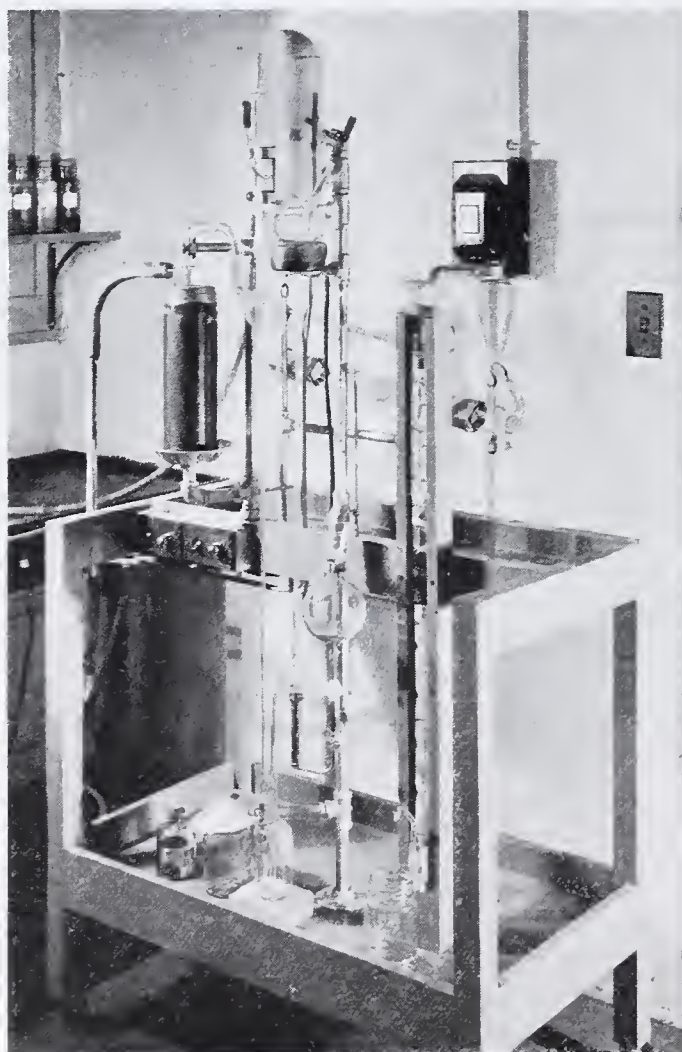


FIGURE 1. GENERAL VIEW OF COMPLETED APPARATUS

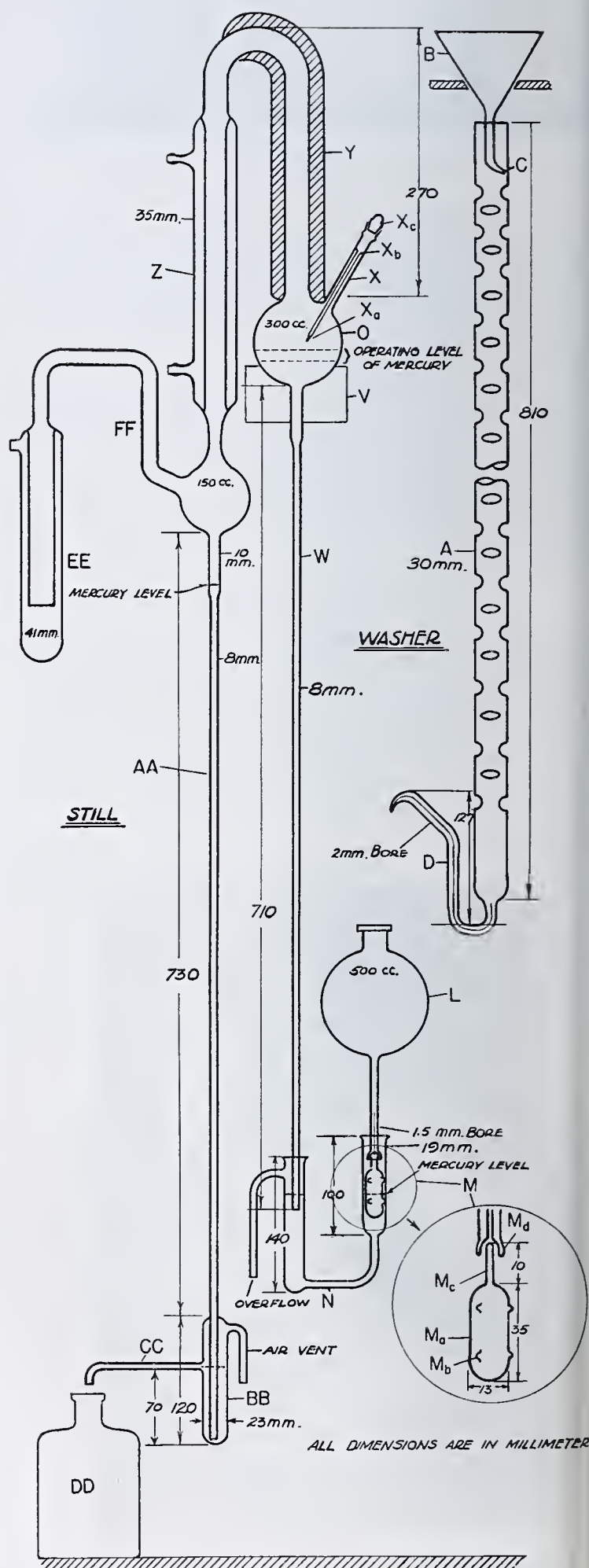


FIGURE 2. WASHING COLUMN AND STILL



There was needed in this laboratory a complete mercury-purification system that was portable and at least semicontinuous, and would furnish mercury of a purity satisfactory for use in diffusion pumps, gages, thermoregulators, etc. It was decided to provide for washing, drying, and distillation with optional aeration. The final assembly contains little that is new, either as to methods of purification or apparatus; however, the assembly has proved so useful and convenient in this laboratory that it is felt a description of a complete unit should be of interest to a number of readers.

### Apparatus and Operation

A general view of the assembled apparatus is shown in Figure 1. Figures 2, 3, and 4 illustrate the design of the component parts, described below.

**WASHER.** The mercury is introduced into the washing column, *A* (Figure 2), through funnel *B* which has the delivery end bent toward the side wall of the column and pulled out to a capillary, *C*. The stream of mercury projected against the wall of the column breaks up into very fine droplets. This is most easily accomplished when the jet of the funnel projects below the surface of the washing liquid. The droplets zigzag through the solution by bouncing stepwise on the indentations formed in the side wall of the column as shown in the drawing. The washed mercury collected at the bottom is delivered to a receptacle through the capillary column, *D*, which is so proportioned as to support the wash solution in the usual manner.

**DRYER.** A top and a front view of the dryer are shown in Figure 3. The washed mercury is transferred to funnel *E* of the dryer and admitted in a 2.25-kg. (5-pound) charge to *F*, which is then somewhat less than half full. The mercury is agitated and dried by pulling warm air (approximately 100° C.) through it. This is accomplished by evacuating the chamber, *F*, by means of a water pump connected to the outlet of trap *G*. This vacuum maintained above the mercury causes air to enter at *GG* below the surface of the mercury and proceed through it in successive bursts which give very effective agitation. Preliminary to passing through the mercury the air is heated by contact with heating coil *J*, which is made of 5.18 meters (17 feet) of No. 28 Nichrome wire random-wound to promote more efficient heat transfer. The incoming air first passes through a filter plug of glass wool held in place by disks of fine-mesh screen cut to fit expanded sections in the glass tube as shown at *H*. The air enters at *H*, is heated in passing through *J*, bubbles through the mercury starting at *GG*, picks up water from it, and goes through the remainder of chamber *F*, through the trap, and out at *G* to the water pump. The dry mercury is drained out through stopcock *K*. No lubricant is used on either of the stopcocks shown. The minimum drying time per charge is 30 minutes.

**STILL.** The dry mercury is put into reservoir *L* (Figure 2) where it is supported by the float valve assembly, *M*. A float valve is used since it automatically maintains a constant level, and can be made entirely of glass. In making it, a piece of small-diameter glass rod, *Mc*, is sealed to bulb *Ma*. The opposite end of *Mc* is ground to a narrow seat at *Md* with the capillary tubing delivering the mercury from the reservoir. The final step of the grinding is done with FFF Carborundum. Six glass knobs, *Mb*, on the surface of the bulb furnish a minimum of frictional contact with the surrounding tube, and thus permit ease of

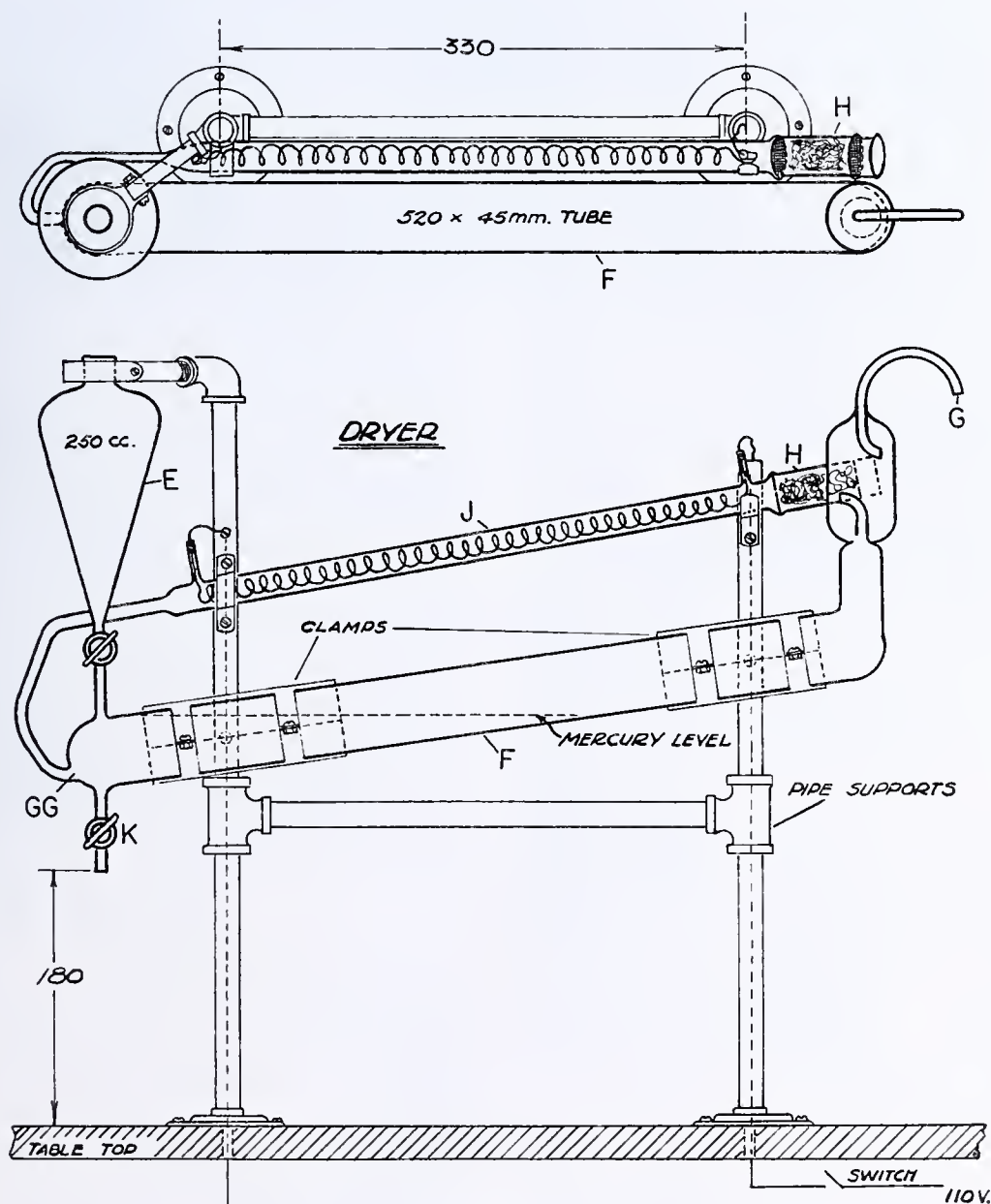


FIGURE 3



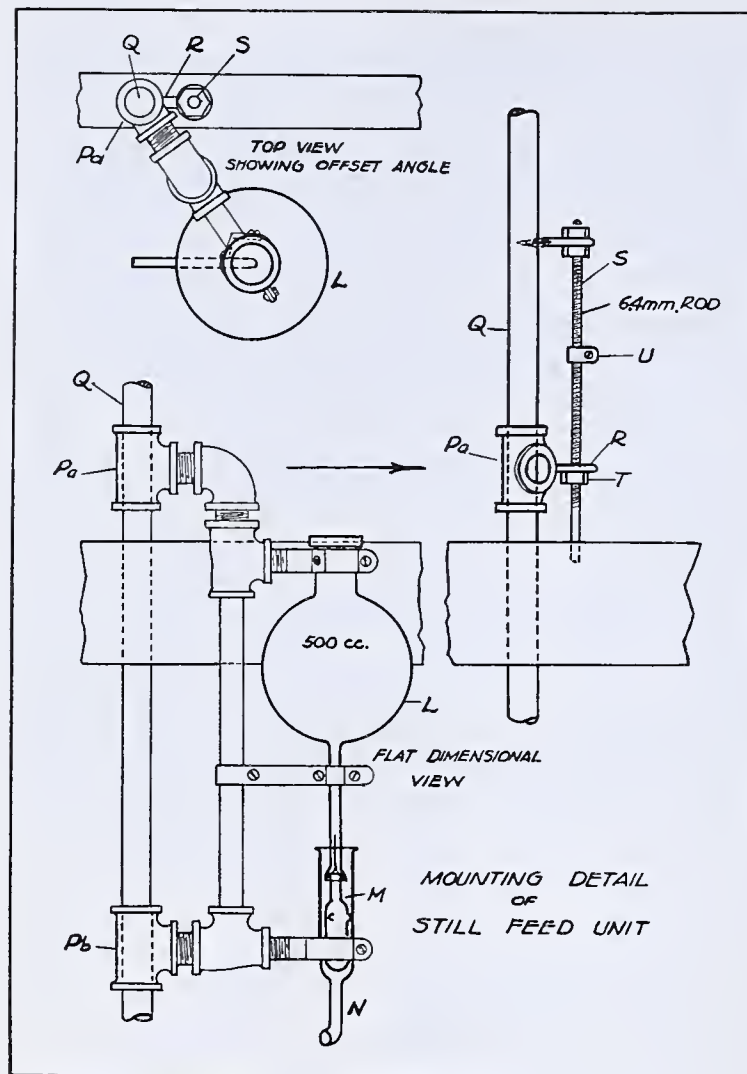


FIGURE 4

movement. The actual dimensions of the float are not critical; with the proportions used here the bulb floats only about 33 per cent submerged in operation. The buoyancy of the remaining 67 per cent acts as a reserve to exert more pressure on the valve in case there is some tendency to stick.

The constant mercury level in both legs of the U-tube, *N*, in turn maintains a constant level in the boiler, *O*. Adjustment for variation in barometric pressure and for pressure changes due to the air leak is made by raising or lowering the assembly of *L*, *M*, and *N* as a unit. This ordinarily needs checking only once a day. Figure 4 shows how these parts are supported and adjusted. *Pa* and *Pb* are pipe tees bored out to make a smooth sliding fit on the supporting standard *Q*, made of 21-mm. outside diameter pipe (standard 0.5-inch iron pipe). A screw eye, *R*, is soldered into the side of the sliding tee, *Pa*; the eye of the screw makes a smooth sliding fit over the threaded support and guide rod, *S*. Adjustable nut *T* is used to hold the assembly at the desired point, while stop *U* limits the upward movement and thus prevents the barometric leg, *W* (Figure 2), from breaking through the bottom of tube *N*. The remaining clamps are made to fit the parts as shown.

Heat is supplied to the boiler by the electric heater, *V*, made by winding 6.1 meters (20 feet) of No. 22 Nichrome wire into a coil on a 4.7-mm. (0.1875-inch) mandrel. The element is coiled into a pancake spiral conforming to the shape of the flask and embedded in Sauereisen electric heater cement (made by the Sauereisen Cements Co., Pittsburgh, Pa.) in a shallow can of convenient size, using a cork as a core to provide a hole in the center for the supply tube, *W*. It is important to oxidize the element before this step, since adjacent turns of a bright wire embedded in cement may short-circuit and burn out the heater. The oxidizing can be done by stretching the coil in the air and running it at full line voltage (115 volts) for about 30 minutes. Using an external resistance of 8 ohms in series with the heater across the 115-volt line, the effective input to the heater is 230 watts.

*X* (Figure 2) is the arrangement for pulling (blowing) air across the surface of the heated mercury when desired. The inner tube is pulled down to a capillary tip, *Xa*. The ring-seal, *Xb*, is made at a distance of about 4 cm. from the flask, so that whenever

necessary the capillary can be removed and replaced easily and without danger of breaking the flask. A carefully ground glass plug, *Xc*, is provided for use when distillation without air is desired. Rather than pass air over the surface of the mercury, some workers prefer to draw air through it. This tends to decrease bumping of the boiling mercury.

The connection, *Y*, to the condenser, *Z*, is made long enough so that no impure mercury can be carried over mechanically in a moment of unexpectedly vigorous boiling. The condensed mercury drops down into another barometric leg, *AA*, which feeds delivery tube *CC* through trap *BB*. Sufficient mercury is held in *BB* to fill tube *AA* to barometric height when evacuating the still in starting a new run. During distillation pure mercury is delivered continuously to a clean dry bottle, *DD*.

Connection to the vacuum pump is through a trap, *EE*, which is surrounded by a dry ice-acetone mixture. Tube *FF* is turned upward to allow the mercury collected in it to drain back.

## Mounting

All the apparatus is mounted on a specially constructed table as shown in Figure 1. The dimensions of the table are: over-all height, including casters, 88 cm.; length, 88 cm.; width, 51 cm.; width of open section in top, 21 cm.; height of bottom shelf, 27 cm. The two shelves are plywood, suitably braced, and placed, as shown in the photograph, to act as trays to catch the small amount of mercury that is inevitably spilled. A small hole placed in a corner of each shelf provides a convenient means for draining. The interior corners of the shelves are rounded to a fillet with plastic wood.

The support for the dryer is made of 17-mm. outside diameter pipe (standard 0.375-inch iron pipe); the remaining supports are made largely of 21-mm. pipe (standard 0.5-inch pipe). Sliding tees fastened by setscrews are used where convenience dictates.

The entire layout is so arranged that all the leads for power, water, drain, and vacuum are at the same end of the table. Separate switches with pilot lights are provided for the two heating circuits.

## Operating Notes

Very oily and dirty mercury is given a preliminary batch washing with acetone and then tap water and strained through a cloth. A pin-holed filter paper is used in funnel *B*. Nitric acid (25 per cent) is used in the column for the first washes. The final washes are with distilled water. No attempt is made here to state the criteria by which the purity of the mercury can be determined. The treatment prior to distillation is naturally governed by the contemplated use of the final product. It is sufficient for the purposes of this laboratory to be guided by the appearance of the mercury in the intermediate steps and by the behavior of the final product when used. Any glass blowing that is done on the system after it has had mercury in it should be done with a dry-ice trap in the line to the blowing tube to protect the worker from mercury vapors.

The rate of distillation at 230 watts input to the heater is 400 to 450 grams per hour. The reservoir is large enough so that the distillation can easily continue 10 hours without attention.

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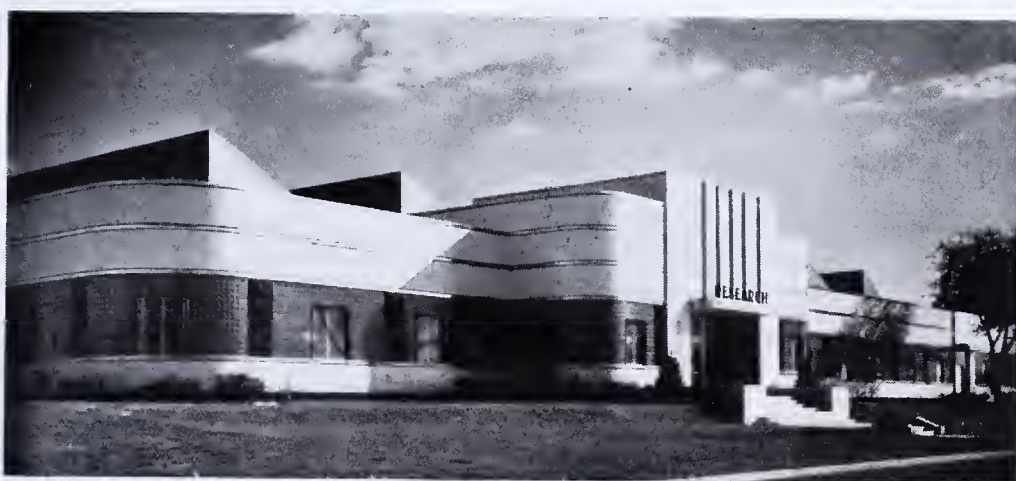


# Modern

# Laboratories

## Armco Research Laboratories

ANSON HAYES, American Rolling Mill Co., Middletown, Ohio



ARMCO RESEARCH LABORATORIES

**T**HE new research laboratories of the American Rolling Mill Co., dedicated at Middletown, Ohio, on November 5, illustrate to an unusual degree the company's own progress in product development.

The building, costing \$280,000, was erected by The Austin Company in coöperation with Harold Goetz, Middletown architect. The exterior is of porcelain-enameled iron, stainless steel, and glass block. The single-story research building, with its sweeping lines, typifies modern industrial design and the role of sheet iron and steel in its application to construction. The Armco laboratories represent the first use of steel walls on a large scale.

The building has a frontage of 255 feet and a depth of 175 feet, providing 43,500 square feet of floor space. It is a sawtooth type with welded steel frame construction of new design. Not a rivet was driven in the structure. A solid concrete wall, 4 feet underground and 1 foot above, forms the foundation. Structural steel is anchored to concrete piers. Main sawtooth columns are 16-inch, 36-pound wide flanged sections, spaced 30 feet apart and supported by columns on 30-foot centers. The spacing, in addition to the elimination of trusses and other shadow-producing crossbars through the use of bent beams and welding, removes virtually all obstructions to the even distribution of light.

The building takes advantage of north light and reduces heating and maintenance expense, since the vertical surface of glass block has high insulating properties and constitutes a self-washing surface. Seven sawtooth faces extend over the width of the laboratory section of the building. The method of installation facilitates air conditioning and elimi-

nates the danger of leakage frequently encountered in sloping sash as a result of expansion and contraction.

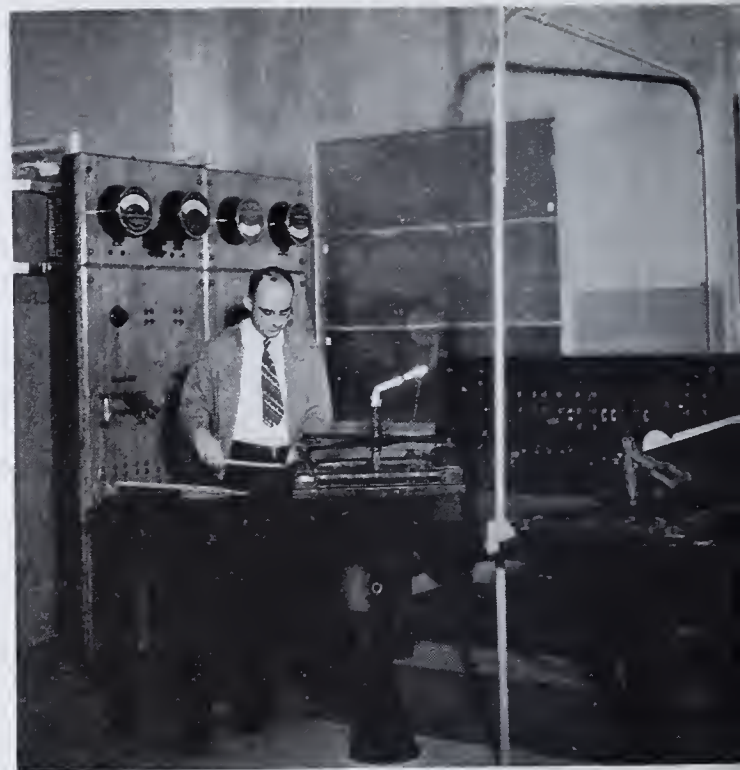
Steelox metal roof panels are 18-gage galvanized iron, with a 5-inch web on 9-inch centers, spanning 15 feet from girder to girder. For acoustical purposes, the metal ceilings of the offices are perforated with about ten holes  $\frac{3}{32}$  inch in diameter for every square inch of surface. The end of each panel is spot-welded to the center of the girder. Pitch of the valleys of the roof is 6 inches for every 12 feet of horizontal run.

Acoustical cork inside the perforated ceiling panels rests on 1-inch metal chairs welded in the center and at the ends of each panel. On top of the cork, 26-gage galvanized corrugated iron sheets, with 0.5-inch corrugations, run at right angles to the web members and are covered with 1-inch insulating cork, fastened down with helical sheet metal nails. To cover the cork, an asphalt material is used in the sawtooth slopes. Tar and gravel are utilized in the valleys and flat decks. Roof drainage is provided by metal roof sumps, draining into 4- and 5-inch downspout lines running down structural columns into the underground sewer system.

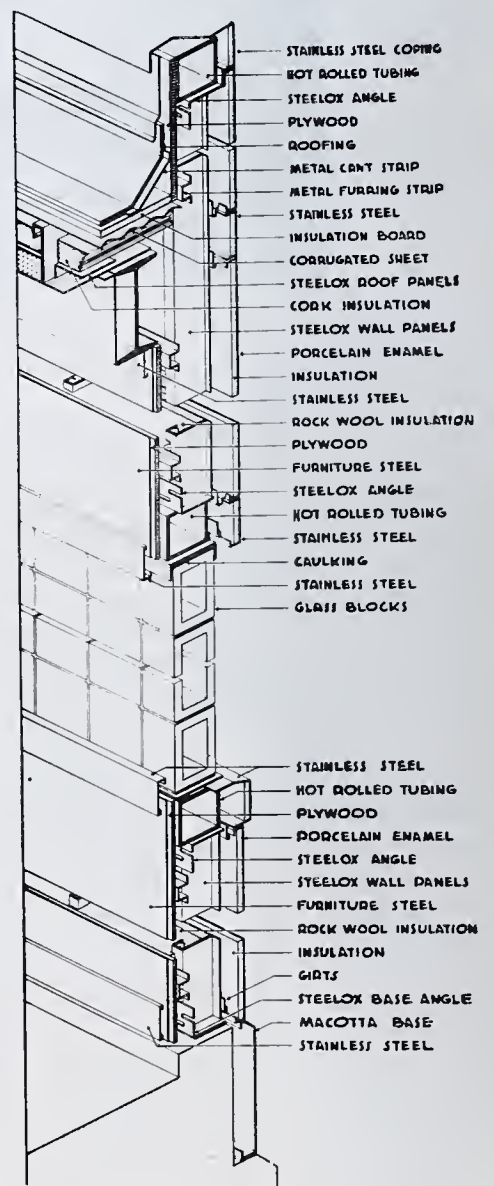
The ceiling of the chemical section is solid metal, with no perforations.

Exterior walls rest on a concrete floor slab integral with the building foundation. Three of the exterior elevations are faced with combinations of porcelain-enameled iron sheets, stainless steel, and glass block. They are formed with 13.6-pound 4-inch square metal tubing, which provides the skeleton for outside walls. Horizontal metal tubes are welded beneath the window sills and above the glass block. Two vertical tubes in each pilaster are fastened to the founda-





MAGNETICS LABORATORY



SPECIAL CONSTRUCTION OF WALL SECTION



tion with anchor bolts. All tubes are welded to the structural frame.

Steelox channel sections (manufactured by Steel Buildings, Inc.) form the nucleus of the wall sections. In all sections except at the glass-block openings, 20-gage galvanized Steelox panels, with flanges facing inward, are bolted to the framework. Each section has a 3-inch channel filled with an insulating material, and covered with 1-inch square continuous hollow metal furring strips, welded to the Steelox webs. Interior walls of the laboratory section are covered with 22-gage flat steel sheets, painted in two shades of gray. The panels have been filled with an insulating material and covered on the inside with 18-gage walnut-finished furniture steel, except where rough shop work dictated the use of painted sheet steel.

The rear wall, sawtooth gables, and most of the partitions in the laboratory section are of the insulated steel wall, developed by The Insulated Steel Construction Company. The wall is formed of two thicknesses of light-gage sheet steel, filled with a special mineral product similar to mica, which possesses high sound-proofing and insulating qualities.

The entire floor is concrete, covered with asphalt tile in the main office sections. All electric, telephone, and other service lines have been placed underground in fiber ducts, which have been encased in the concrete floor and are accessible through manholes every 200 feet. Controls are grouped, with a main distribution center at the switchboard, in the center of the laboratory section.

Ventilation and atmospheric conditions are controlled by two air-conditioning systems, one for the research staff offices and one for the testing shops and laboratories. There are five units, two of which provide zone control for northern and western exposures. The laboratory section is conditioned by three units, each providing zone control in a self-contained group of rooms, supplemented by fume- and heat-exhaust systems in chemical laboratories. Deep well water is used for summer cooling.

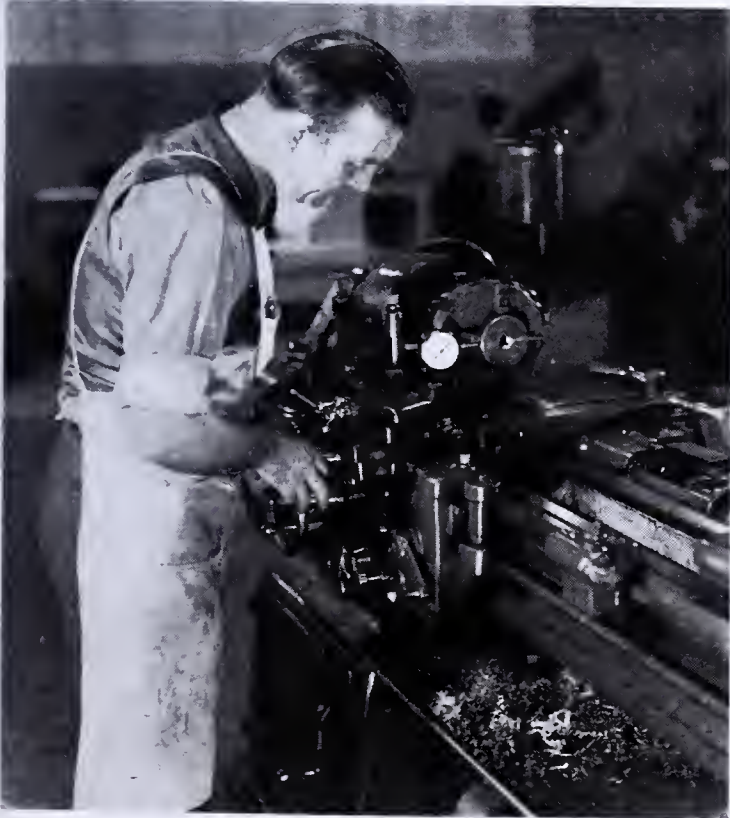
Each unit is suspended on a structural-steel subbase extending completely under the face and by-pass dampers, the cooling coil, the heating coil, the fan, and motor. The units are cased in galvanized Armco ingot iron. Supply and return air ducts to all parts of the building are made of 24- and 22-gage galvanized Armco ingot iron.

Fresh-air intakes are set in the glass-block sawtooth walls and conditioned air is supplied to rooms through diffusing grilles placed near ceilings. The return air is recirculated from rooms through grilles near the floor and the ceiling. All units are located overhead in the peaks of the sawtooth roof to provide ample clearance for testing machinery. Horizontal duct work is run overhead, flush with partitions or structural members so as to be inconspicuous.

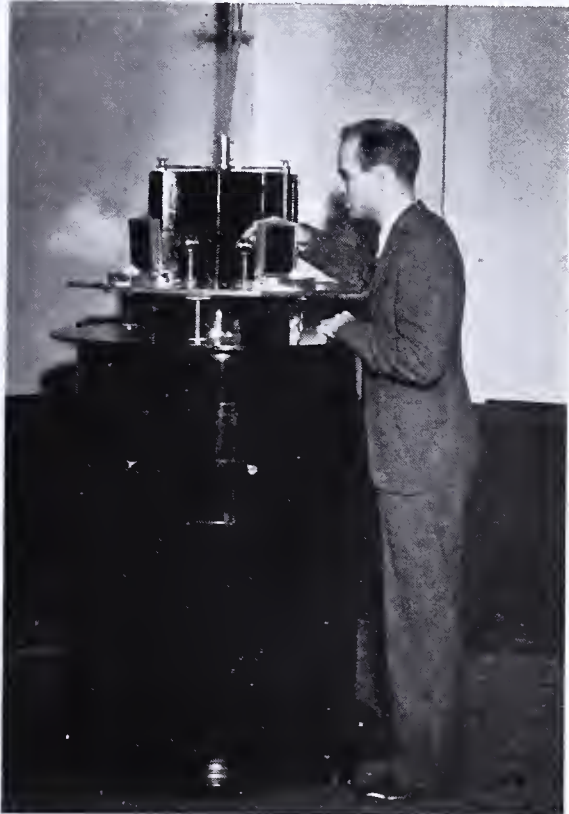
The office units are designed to maintain a summer dry-bulb temperature of 80° F., with a relative humidity not exceeding 50 per cent, and a winter dry-bulb temperature of 70° F., with a relative humidity of 30 per cent. Because of the highly insulated wall and roof construction, the relative humidity in winter is considerably above that for the average building.

Twelve laboratories with complete facilities for specialized research provide equipment for tests to determine and maintain the quality of all Armco products. These include equipment for tests of welding methods for special analysis and stainless steels; for development of corrosion-resistant sheets and strip, iron sheets for porcelain enameling, high-finished sheets for deep drawing, sheets for electrical uses, and zinc and other metal coatings for sheets; and for development of nonmetallic coatings and the improvement of surfaces to hold these coatings; as well as for blast furnace, open hearth, and electric furnace experiments.

There are four chemical laboratories in the building, as well as a sample room and a stock room. One laboratory is used for general analytical work, two for analysis of ferrous and nonferrous alloys and special experimental work, and the fourth for special work. The building is equipped with



LATHE FOR CONSTRUCTING RESEARCH APPARATUS

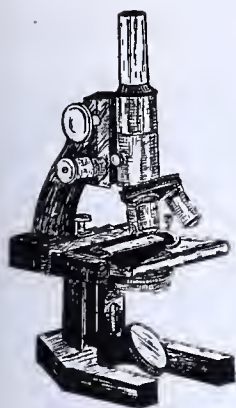


X-RAY DIFFRACTION MACHINE









# Microchemistry

## An Electric Furnace for Automatic Combustion in Microelementary Analysis

L. T. HALLETT, Eastman Kodak Co., Rochester, N. Y.

FOR the past few years work has been done in these laboratories on adapting micromethods to the rapid and accurate routine elementary analysis of organic compounds. The electrical heating of combustion tubes (4) has proved satisfactory and convenient. It has been found that a large portion of the time required to complete an analysis is taken up with the constant attention required in moving the furnace which burns the sample. An even burning by hand manipulation is often difficult and tiresome. By making this part of the analysis automatic, more time for calculation, weighing, or titrating is given and, therefore, a greater number of samples can be analyzed per day with less fatigue.

### Description of Apparatus

**FURNACES.** The electric furnace is simple in design and the construction involves a minimum of machining. The furnaces are of the split type and can be tilted back away from the combustion tube. The materials used for construction are aluminum alloy and stainless steel. Figure 1 gives a general view of the apparatus.

It shows the large furnace, A, in a position corresponding to that over a combustion tube (not shown in the figure) and the

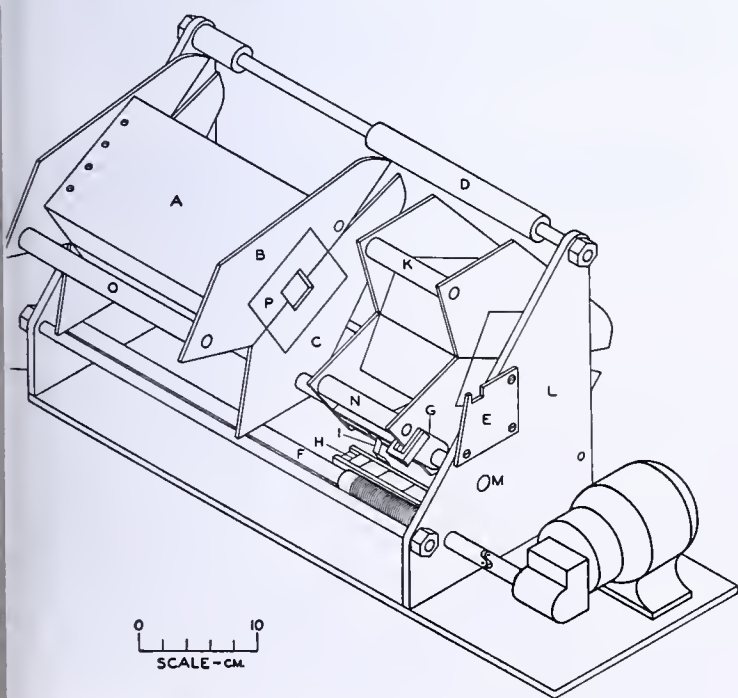


FIGURE 1. GENERAL VIEW OF APPARATUS

small furnace tilted back away from the tube. Combustion tubes, in all cases, are of clear fused quartz having an outside diameter of 9 mm. and an inside diameter of 7 mm. The furnace shells are so made that the ends are in the form of a 10.1-cm. square.

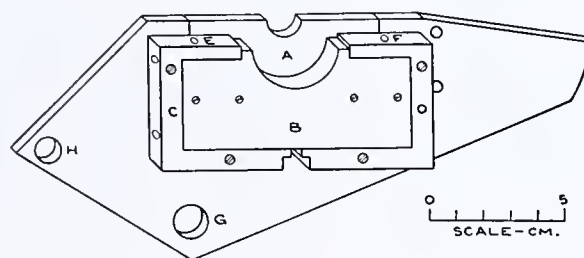


FIGURE 2. END PLATE OF COMBUSTION FURNACE

Figure 2 shows a bottom end plate. There are two such plates (Figure 1, B and C) for each end of the furnace unit. The three sides of each half-section are made of 1.6-mm. thick aluminum and are attached by means of screws to two pieces of aluminum (Figure 2, C and D). The top and bottom halves are hinged at the back and each section contains a refractory unit. The furnace shells are insulated with shredded asbestos packing. The furnaces are so arranged that they are attached to one rod at their base at a point (Figure 1, M, and Figure 2, G) such that, on pushing away from the combustion tube, they describe an arc which allows both top and bottom sections to clear the combustion tube. The dimensions can be obtained from Figures 1 and 2. Rods K, N, and O are made of a material which is a poor heat conductor, such as Synthane, and allow the hot furnaces to be opened and closed without burning the fingers. Figure 2, H, shows the hole into which the Synthane rod fits.

**REFRACTORY UNIT.** The refractory unit is the same as that previously described (2). It consists of an alundum tube with a 2.5-cm. bore and a 3.2-mm. wall cut to form two semicylindrical pieces (Figure 3, B). At the end of the shell and held in place by the two pieces of aluminum (C and D, Figure 2) is placed transite or pressed asbestos, B, 6.4 mm. thick, machined to fit and support the semicylinder of refractory. Another piece (Figure 2, A and Figure 1, P) of asbestos 3.2 mm. thick is inserted in the end plate. Figures 1 and 2 show the dimensions. The 6.4-mm. asbestos is fastened by means of screws to the end plate and the 3.2-mm. is, in turn, fastened to the 6.4-mm. asbestos. The terminals (Figure 3, H and I) of the electric heating elements are fastened into the asbestos and are placed on the sides near the large end plates (Figure 1, L and R). On either side of the alundum semicylinder (Figure 3, B) are placed alundum pieces, A and E, 4.8 mm. thick held in place by screws. Figure 2, E and F, shows the support for these pieces. The heating element consists of No. 24 Ni-chrome wire wound in the form of a pencil coil with a 3.2-mm. inside diameter and supported on a 3.2-mm. diameter alundum rod which fits inside the coil, thus giving it rigidity. There are two of these elements running lengthwise of each half-section of the furnace and connected to binding posts at the end (Figure 3, C and D). The coils thus radiate their heat onto the combustion tube.



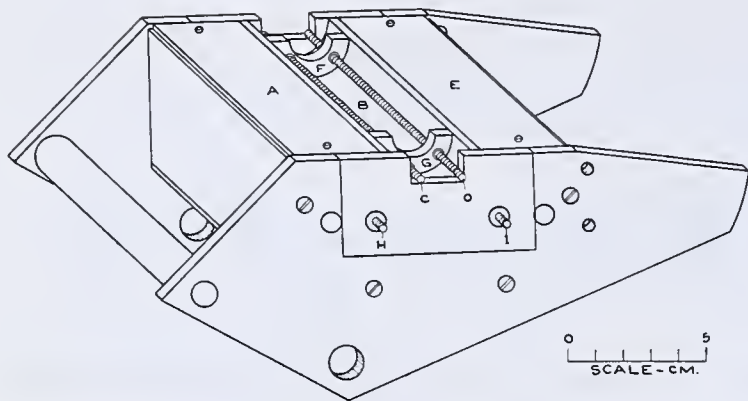


FIGURE 3. REFRACTORY UNIT

The heating element rods with coil are held in place by two small 6.4-mm. thick semicircles of refractory notched to accommodate the heating elements and hold them in place against the alundum refractory tube (Figure 3, *F* and *G*). They are also notched to accommodate the combustion tube. The top half-section has been removed in Figure 3. The furnace temperature is calibrated with a thermocouple and a suitable resistance is placed in the circuit to maintain the desired temperature. The average temperature is 700° to 750° C.

**MOUNTING OF FURNACES.** The base plate on which the apparatus is mounted is 50.8 cm. long by 17.8 cm. wide by 4.8 mm. thick. On this plate are placed two end plates of 6.4-mm. aluminum, 38.1 cm. apart, 24.1 cm. high, and 17.8 cm. wide. At a point 5.7 cm. from the base, the plate is cut at an angle of 40°. One of these end plates is shown in Figure 4. The end plates are fastened by screws to the base plate and are held rigid by a 9.5-mm. rod at the top and two at the bottom, one 9.5 mm. and the other 6.4 mm. in diameter. The position of the rods can be seen in Figures 1 and 4. The 6.4-mm. rod acts as a stop for the furnaces when in the position away from the combustion tube.

The large end plates are also drilled to support two 1.3-cm. diameter stainless steel rods, one of which supports the furnaces and on which they are free to move (Figure 1, *M*). The other (Figure 1, *F*) 1.3-cm. shaft has at one end a case-hardened, threaded sleeve 1.9 cm. in diameter, 7.6 cm. long with 18 threads to the inch. This shaft is connected to a Bodine motor (1/80 h. p., Universal type, gear reduction 1120-1) by means of a Universal joint. The motor is bolted to the base plate on the remaining 12.7-cm. space outside the end plates. To the bottom small burning furnace is bolted a segment of screw (Figure 1, *G*) which meshes with the screw on the revolving shaft when the furnace is brought over the combustion tube. As the shaft revolves, the furnace moves forward. All bearings subject to wear have steel bushings. The combustion tube is supported by a notched plate attached to each large end plate (Figure 1, *E*). The top bar which is shown in Figure 1, *D*, provides a safety device so that the furnaces cannot be pushed back until they are opened. Should the small furnace tend to "ride up" on the screw, a piece of brass, weighing about 200 grams, placed inside the upper half of the furnace shell, will prevent this.

**ELECTRICAL UNITS.** The electrical connections for the heating units are situated at one end of the furnace (Figure 5). The furnace which burns the sample has an insulated brush contact on the bottom (Figure 1, *I*). When the furnace is opened and brought over the combustion tube, it makes contact with a brass segment which starts the motor; the proper speed is maintained by means of a suitable resistance in the circuit. At the same time the furnace meshes with the revolving shaft and so moves for-

ward. The initial speed for average burning is 2.5 cm. in 15 minutes. After the furnace has passed over the boat and the sample has carbonized, the brush contact reaches another brass segment which increases the speed to 2.5 cm. in 3 minutes. When the small furnace has reached the end of a predetermined point, which is the large furnace, it is so adjusted that it runs off the screw and makes contact with a segment which allows the motor to run at slow speeds. This last segment is usually of such a length that the final 1.3 cm. that the furnace moves is at this slow speed.

The segments are mounted in a strip of Synthane which, in turn, is supported at a suitable height by means of small bolts screwed into the base (Figure 1, *H*). Some compounds sublime or distill as the furnace moves forward and, if the speed of the furnace at the end of the burning is too fast, the compound will burn explosively or incompletely. By having a final slow speed, they dissipate slowly and are completely burned. The slow speed is attached to a variable 350-ohm Ward Leonard resistance (Bulletin 1103), so that the speed of burning may be varied as required. Figure 6 gives the details of the motor wiring. By varying the position, length, and number of the segments, the peculiarities of burning for carbon, hydrogen, nitrogen, sulfur, and halogen may be met.

The whole unit is mounted on an oak board, 121.9 by 35.5 by 2.5 cm. The board has a 5.1-cm. strip on the bottom on three sides, the back being left open. The electric wires may then be run underneath the board and are readily available for changes or repairs.

## Applications

**DETERMINATION OF HALOGENS AND SULFUR.** Figure 1 is the drawing of the apparatus used for the determinations of halogens and sulfur. The furnace heating the platinum contacts is 17.8 cm. long. The burning furnace is 7.6 cm. long. The space allowed between the two combustion furnaces at the start of a run is 6.3 to 7.6 cm. Three contact segments are generally used: the first for slow or initial burning, the second, fast after the sample has carbonized, and the third, slow for the final 1.3 cm. of travel.

The regular Pregl combustion tube with the glass spiral at the end can be used, but a modified tube, which will be described in a later paper, has the advantages of simpler operation and of an essential saving of working time (3).

The time for combustion of the sample is about 20 minutes. Twelve iodine determinations may be made per day, including calculating. The chlorine and bromine determinations require slightly more time for titrating and, in the case of sulfur, for precipitating and weighing the barium sulfate, but, of course, the burning time is the same in all cases. Iodine is determined by the Goldberg method (1). Bromine and chlorine are determined by the Volhard method and sulfur by the absorption of the oxides in dilute hydrogen peroxide and the precipitation of barium sulfate.

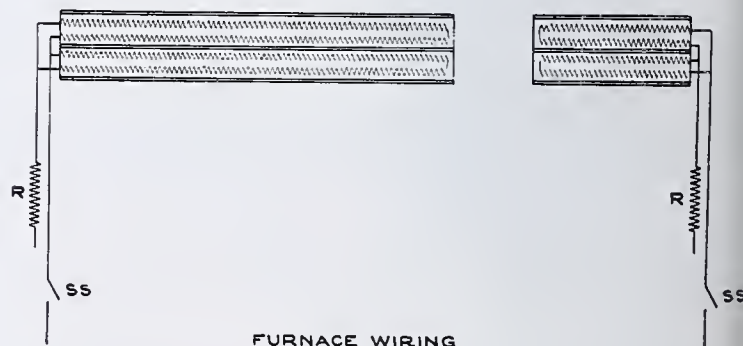


FIGURE 5

**DUMAS NITROGEN.** The changes in apparatus necessary when determining nitrogen according to the Dumas method are: an increase of 3.8 cm. in the over-all length of the frame so that the large furnace is 21.6 cm. in length and the inclusion of four segments—(1) a fast speed to bring the furnace up to the burning position, (2) a slow burning speed, (3) a fast



speed, and finally (4) the last 6.4 mm. a slow or idling speed. Segment 3 is so arranged that by means of a switch it may be thrown into the slow burning speed, 2, if the sample has not burned completely while passing over 2. In the case of liquids where the length of the capillary and its position cannot conveniently be the same each time, the furnace must be watched occasionally to maintain proper burning conditions. The slow speed as before may be varied by a rheostat. Solids rarely require attention. To complete a run requires 30 to 35 minutes. Nine determinations can be done in an 8-hour day, including calculating and weighing out the samples for the next day.

**CARBON AND HYDROGEN.** In the determination of carbon and hydrogen, some laboratories now use electric furnaces for heating that section of the tube containing the lead dioxide filling and the copper oxide-lead chromate mixture. A unit for the automatic combustion of the sample in such a case can readily be built. It consists of only the sample-burning furnace and the mechanism for moving it along the combustion tube. Figure 7 shows such a unit. The frame is the same except that it is shorter. The furnace is round instead of square, and the safety bar at the back is eliminated. The screw is 10.1 instead of 7.6 cm.

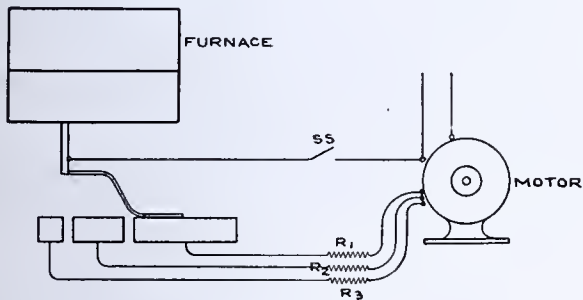


FIGURE 6. MOTOR WIRING

It is provided with 3 speeds: slow initial speed, fast, and then slow. A 350-ohm variable rheostat allows the slow speed to be changed if burning conditions are not suitable. With this apparatus, nine carbon and hydrogen determinations may be done in an 8-hour day, including calculating and weighing out samples for the next day.

**Conclusion**

The automatic combustion unit has allowed an average increase of 25 per cent in the number of analyses completed per day and the strain occasioned by the constant attention during the burning of the sample has been eliminated.

**Summary**

An apparatus using electric furnaces of new design for the automatic combustion of microsamples is described. The furnaces fabricated from aluminum alloy are of the split type and may be conveniently opened and pushed aside so that the combustion tube may be cooled if necessary. A small electric motor with gear reduction drives a screw which in turn moves the sample-burning furnace along the combustion tube. By means of a brush contact passing over a series of insulated metal segments, the speed of the furnace is automatically varied to give slow initial burning and accelerated burning after the sample has carbonized. The furnace automatically stops when it has reached a predeter-

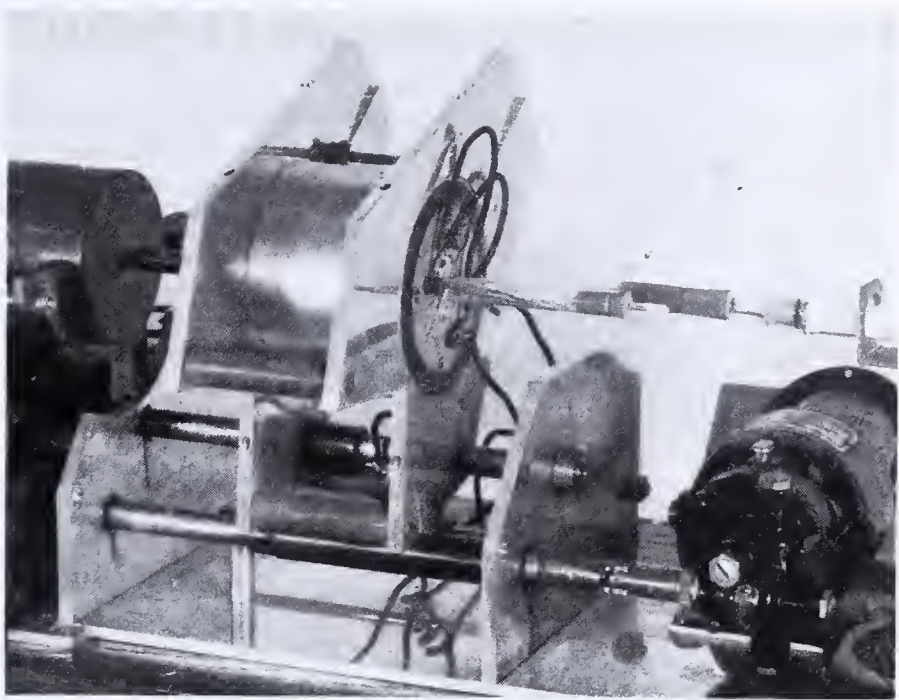


FIGURE 7. UNIT FOR AUTOMATIC COMBUSTION

mined point after the sample has been burned. The application of this type of furnace to such determinations as carbon, hydrogen, nitrogen, halogen, and sulfur is described. The unit is designed primarily for laboratories having a large number of routine determinations. As the combustion of the sample is done automatically, the operator has more time to carry out calculations, titrations, and weighings. About 25 per cent more work can be done per day than is possible with burning the sample by hand, and the operator is less fatigued.

**Acknowledgment**

The author wishes to thank Mr. Ord, in charge of the Research Laboratory instrument shop, for working out the details of the design. Without his continued help, the simplicity of the design could not have been achieved.

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**Correction**

In the article entitled "A New Method in Pycnometric Analysis" [*IND. ENG. CHEM., Anal. Ed.*, 9, 592 (1937)] two term definitions have been confused. Under the heading "Theory" the definitions should read:

- $A$  = weight of pycnometer plus precipitate plus liquid necessary to fill pycnometer
- $V$  = capacity of pycnometer
- $d$  = density of precipitate in grams per cc.

W. WALKER RUSSELL



# The Microtechnic of Organic Qualitative Analysis

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THE field of analysis which has received perhaps the least attention from microchemists, and which at the same time offers the greatest opportunity for a demonstration of the economy of time, energy, and materials which micro-methods can effect, is qualitative organic analysis.

Most of the reactions and operations in organic analysis require much more time than the corresponding inorganic procedures. This is due not only to the greater speed of ionic reactions as compared to the reactions of organic substances (often not even in the same phase) but also to the greater complexity of the materials dealt with in organic work. Any procedures, therefore, which cut down the time required for the operations used in qualitative organic analysis should be welcomed. It is the intention of the authors in this series of papers to indicate how micromethods can be utilized to this end.

Figure 1 will indicate the saving which can be effected with microprocedures. The apparatus shown is the simplest distillation setup, for both the macro and the micro operation. Actually the separation will be more complete with the microtube of Emich (shown in the lower center of the drawing) because an actual fractionation is carried out.

It is not the authors' intention to develop a new scheme of analysis but to adapt the microtechnic to one of the existing systems. In their opinion a system based upon a general classification of organic compounds according to a definite physical property such as the scheme of Kamm (21), Staudinger (31), or Shriner and Fuson (30) is to be preferred to one which classifies compounds only according to their constituent elements. The procedure, therefore, is based on the system of Kamm except where micromethods make it possible to omit a step or two.

The micromethods developed thus far in organic qualitative analysis have been confined almost exclusively to specific tests for some compounds and, although they include some of the oldest tests known to microchemistry, such as Wormley's test for poisons (33), most of them are for the less common compounds such as alkaloids.

The steps in the scheme of analysis adopted are as follows: preliminary physical examination and purification, determination of physical constants, qualitative tests for the elements, determination of solubility behavior, homologous tests, consultation of literature, and preparation of derivatives.

## Preliminary Examination

The unknown substance should be examined for homogeneity, color, odor, and crystalline structure. A microscope or lens will be of great assistance in this examination.

If a polarizing microscope is available, impurities which may be very much like the rest of the material in color and

shape can sometimes be detected by the difference in behavior to polarized light.

If the substance is nonhomogeneous, it must be purified before the physical constants can be determined. In the case of solids, recrystallization or sublimation is resorted to, and in the case of liquids fractional distillation usually suffices (6, 26).

**IGNITION TEST.** It has been found in a series of experiments that the ignition test gives as much information when carried out on a microscale as when larger quantities of the substance are used. The test is carried out by placing a crystal (about 0.01 mg.) on a platinum microspatula (made by flattening one end of a No. 20 platinum wire for a distance of about 5 mm. and fixing the wire in a glass rod or needle holder) and holding it in the colorless flame of a microburner (Figure 2). It is desirable to use one of the adjustable types of microburners, since they give a much finer and smaller flame. The sample should not be held directly in the flame, but the wire should be heated about 1 cm. from the flattened end and then moved so that the sample is gradually brought into the flame. This will prevent loss of the sample by spattering.

This procedure will give the following information:

1. An approximate idea of the melting point or sublimation point, if the substance melts or sublimes, can be obtained.
2. When the substance begins to burn, the nature of the flame should be observed. If it is smoky, an aromatic compound is indicated. The luminosity of the flame is also sometimes of aid in classifying a compound. If the substance explodes (sputters) this fact should be noted, together with the odor of any vapors.
3. If any residue is left after ignition, this may be identified. Since this is in most cases an alkali or alkaline earth carbonate, the residue should be tested for alkalinity by dissolving in a drop of water on a microscope slide and touching the drop with a fiber of litmus silk (11). Identification of the metal can be carried out either by a flame test or, in case it is not an alkali or alkaline earth metal, by a systematic qualitative analysis (2). The presence of a metal indicates, of course, a salt or organo-metallic compound.

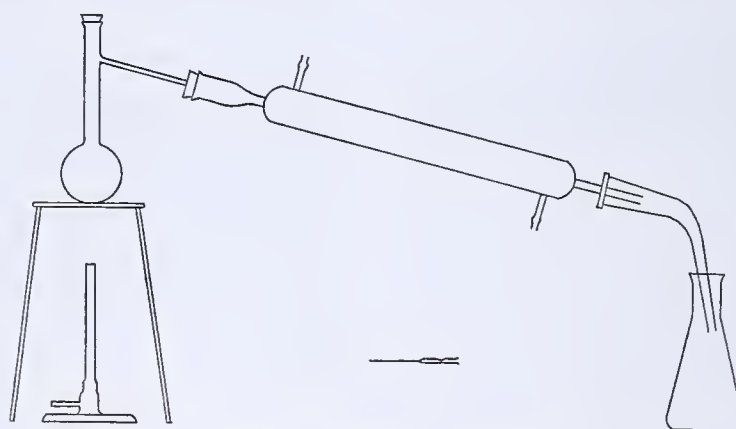


FIGURE 1. MACRO AND MICRO DISTILLATION SETUP

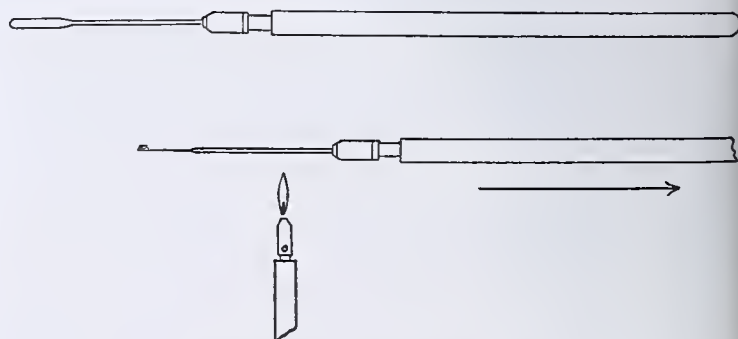


FIGURE 2. IGNITION TEST



## Determination of Physical Constants

The final identification of a substance, whether the original compound or one of its derivatives, may be made by the determination of its physical constants or by a study of its crystalline form under the microscope.

The physical constants usually employed include boiling point, melting point, density, refractive index, optical rotation, and molecular weight. Of these the first three are important, the others being used only for confirmation.

**MELTING POINT.** The melting point may be determined in the usual way, since only a few milligrams or less of the substance are required. For smaller quantities the Kofler-Hilbck electric hot stage (22) can be used. Only a single tiny crystal is required. (Inasmuch as observation under the microscope enables one to determine more accurately when the substance is beginning to melt, the melting point as determined by the use of such a stage will be a little under the value given in the literature.) Blocks of aluminum or copper have been recommended for use in place of the ordinary heating bath (3, 23, 27).

**BOILING POINT.** The method of Emich (7) gives highly accurate results in the determination of the boiling point. Hays, Hart, and Gustavson (20) describe an apparatus for determining the boiling point at altitudes other than sea level.

**DENSITY.** If sufficient amounts of material are available (0.5 to 3 mg.) and a microbalance of either the Nernst or the Juhlmann type is used, a micropycnometer will serve for the determination of the density of liquids (25). In the absence of a microbalance, the suspension method of Emich (14) can be employed. (See also 4. Several micromethods for the determination of density of solids and liquids and also a review of the literature on this subject are given by Willard and Blank, 32.)

**REFRACTIVE INDEX.** The refractive index of liquids can be determined in the usual way with an Abbe or dipping refractometer. With very small amounts of liquids or solids, the immersion method (10) can be used. A list of suitable liquid and solid standards can be obtained from any book on microscopy petrography. In some cases the *schlieren* method of Emich (8) can be employed to advantage.

**SPECIFIC ROTATION.** The specific rotation can be measured either by the method of Donau (5) or Fischer (18).

**MOLECULAR WEIGHT.** A number of methods are available for the determination of the molecular weight on a microscale. The Rast method (16, 24) is very simple and can be used for all solids and many liquids. Only a fraction of a milligram of sample is used. The osmotic method of Barger can also be used (15). The method of determining the molecular weight by a vapor density measurement has been developed by one of the authors (28).

**OTHER PHYSICAL CONSTANTS.** Other constants which can be used for the identification of a crystalline organic substance are the interfacial and silhouette angles (29).

## Elementary Analysis

Although microchemical tests for both hydrogen and carbon have been described (12), it is assumed that only organic compounds are being analyzed and tests for these elements can be omitted.

Emich (13) describes two methods for the detection of nitrogen in organic compounds—the sodium fusion and the ammonia test. While the sodium fusion when carried out on a microscale greatly facilitates the destruction of the excess sodium and eliminates the danger of an explosion, it is rather difficult to get the tiny pieces of sodium into the capillary. Furthermore, the possibility of nitrogen escaping as the free gas (19) or, in the case of highly volatile compounds, without decomposition of the sample (17) exists in the microtest as well as the macro. The ammonia test, of course, cannot be applied to all nitrogen compounds.

The authors have turned to the magnesium-potassium carbonate fusion method as modified by Barkenbus and Baker (1), and have developed the following microtechnic:

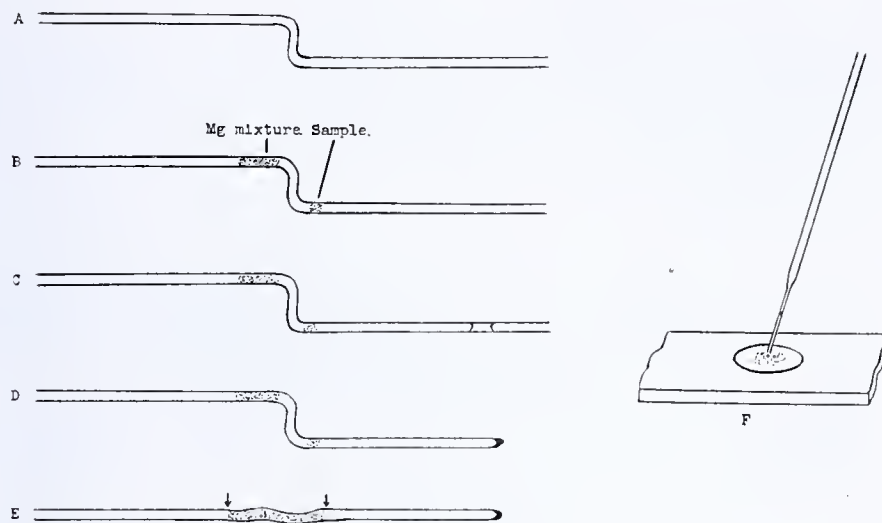


FIGURE 3. DETECTOR OF NITROGEN, SULFUR, AND HALOGENS IN ORGANIC COMPOUNDS

A capillary tube of Pyrex glass of about 1-mm. bore is bent as shown in Figure 3, A. The magnesium powder-potassium carbonate mixture (1 part of magnesium powder ground in an agate mortar with 2 parts of anhydrous potassium carbonate) is introduced at one end and packed in with a glass thread, so that the full cross section of the tube is filled. The layer of carbonate mixture should be about 5 mm. long, B. The sample (0.1 to 1 mg.) is introduced into the other end, which is then dipped into a vial of ether so that a droplet of ether about 2-mm. long rises in the tube by capillary action, C. In the case of liquids, the ether must be introduced before the sample. The tube is then sealed at the sample end by heating in a microflame and pinching the softened glass with a forceps. The ether evaporates during the sealing, the vapor displacing the air in the tube. The portion of the tube containing the carbonate-magnesium mixture is heated in the microflame to glowing, after which the tube is held in a Bunsen flame so that both the magnesium mixture and the sample are heated at the same time. In this way the sample is distilled over the glowing mixture. While the tube is still hot and soft, it is pulled out into a straight tube.

After cooling, the tube is cut at the points shown in E. The piece containing the fused mass is placed in a depression of a spot plate which has been previously moistened, and is crushed, preferably with a porcelain spoon or the small end of a porcelain pestle. The moisture film on the plate will prevent the pieces from flying off the plate. A drop of hot water is then placed on the residue and, after being allowed to stand for a few minutes, it is drawn off into a fine capillary pipet, the point of which is too fine to permit the solid to be drawn up with the liquid. In case any solid particle is drawn up with the liquid, the pipet is sealed at the other end, the liquid and solid are centrifuged to this end, the capillary is cut just above the surface of the liquid, and the clear centrifugate is drawn off in another capillary pipet. This clear liquid is used for the tests for nitrogen, sulfur, and the halogens.

**NITROGEN.** A drop of ferrous sulfate solution is added to the test drop on a slide. After being stirred and allowed to stand for a minute, the clear liquid is drawn off into a capillary pipet, and blown out on a white spot plate and a drop of concentrated hydrochloric acid is added. The Prussian blue color indicates nitrogen.

Professor Barkenbus has kindly made the following suggestion regarding the test for nitrogen in the presence of sulfur. He and Mr. Baker have found, and the authors have confirmed this with the microtest, that when both sulfur and nitrogen are present the test for nitrogen by means of the ferrocyanide reaction becomes doubtful. If, however, the filtrate from the fusion mixture is first tested for the presence of sulfur and then, if this test is positive, for nitrogen by means of the ferric thiocyanate test, a red coloration will appear if nitrogen is also present. The thiocyanate test is carried out by adding a drop of ferric chloride solution to the filtrate from the fusion mixture.

**HALOGEN.** The test drop is acidified with nitric acid by inverting the slide on which the drop rests over a bottle of concentrated nitric acid. Silver nitrate is then added either in the form of a tiny crystal or as a drop of the solution. Care must be taken not to touch the portion of the combustion tube containing the fusion mixture with the fingers, since sufficient chloride is left on the glass from the contact of the fingers to give a positive test for this element. This portion of the tube should be handled only with the forceps in any case. In case a positive test for the halogens has been obtained, it is advisable to make further



tests to obtain an indication of the type of halogen compound under consideration. Details of this procedure will be given in a subsequent report.

**SULFUR.** The drop of test solution is acidified with acetic acid and a drop of lead acetate is added. The precipitate is observed against a white background. A black precipitate of lead sulfide indicates sulfur.

The compounds used in testing this procedure include:

**Nitrogen:** urea, benzamide, carbazole, dinitrostilbene disodium disulfonate, dimethylaniline, benzonitrile, nitrobenzene, nicotine, phenylhydrazine, pyridine, 1-naphthylamine, *p*-toluidine, picric acid, aminoazobenzene hydrochloride, and asparagine.

**Sulfur:** thiourea, benzenesulfonyl chloride, dinitrostilbene disodium disulfonate, and carbon disulfide.

**Chlorine:** Dichlorobenzene.

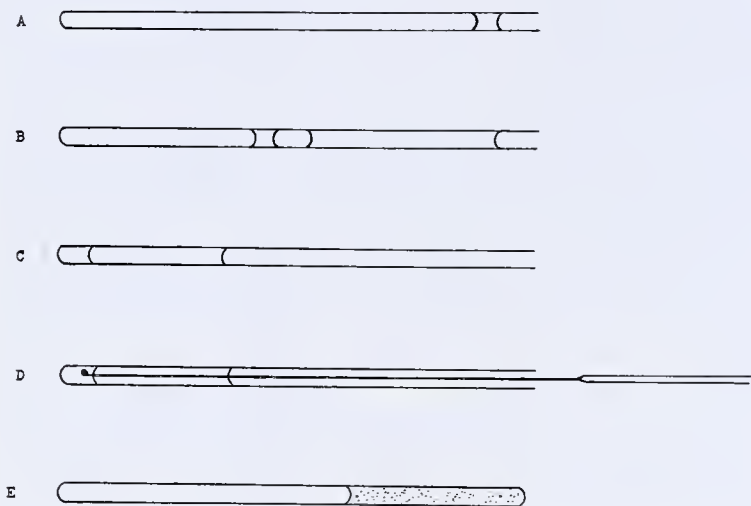


FIGURE 4. CAPILLARY DETERMINATION OF SOLUBILITY

It is recommended that the potassium carbonate-magnesium mixture be made up fresh frequently, since it becomes moist and cannot be handled as readily as when dry.

In the case of explosive substances such as picric acid, the sample should be heated very carefully; otherwise it might explode and blow out the contents of the tube. These explosive substances can be detected when carrying out the preliminary ignition test.

### Determination of Solubility Behavior

The procedures of Kamm and others mentioned above are based on the division of organic compounds into several large groups according to their solubility in a variety of solvents. The particular solvents employed differ to some extent in the various schemes, but the actual technic remains the same.

Since there is no sharp dividing line between "soluble" and "insoluble," an arbitrary ratio of solute to solvent must be set. Again this varies according to the solvent employed and the physical state of the solute, but an average value is 1 part of solute to 25 parts of solvent. If this ratio is exceeded the compound is designated as "insoluble"; if it is less than this value it is designated as "soluble." Borderline cases are placed in two classes and tested for in each. The ratio of solute to solvent may be determined either by adding increments of the solvent to a fixed quantity of solute, or vice versa, whichever is more convenient.

Work on solubility tests has not as yet been extended to a large variety of compounds, but the general technic has been worked out. Two technics have been developed for the determination of solubility behavior on a micro scale. The first uses the capillary, the second the *schlieren* cell. Both methods may be used with slight modifications for either solids or liquids.

**CAPILLARY METHOD.** In order to determine the solubility behavior of a liquid, a capillary tube of about 0.5-mm. bore and 70 mm. long is dipped into the sample until a droplet about 2 mm. long (0.1 cu. mm.) is drawn up (Figure 4, A). The capillary is then dipped into the solvent until a droplet about 10 mm. long is drawn in, B. The end of the capillary is sealed and the solvent and solute are centrifuged to the closed end.

The solute and solvent may now be mixed in one of two ways. In the first, a glass thread with the end fused to a droplet, D, is inserted into the capillary and the two liquids are stirred by drawing the thread in and out of the tube and at the same time twirling it between the fingers, thereby giving it a rotary as well as a translatory motion. The second method of mixing consists of sealing the open end of the capillary and centrifuging the liquids back and forth from one end of the capillary to the other. In this way the liquid of greater density is always thrown to the end of the capillary and on being centrifuged to the other end must pass through the lighter liquid. Complete and thorough mixing is thus obtained.

By either method of mixing, the degree of solubility is determined by examining the resulting droplet. If it is perfectly homogeneous and clear, the liquids are completely miscible. If the droplet appears turbid or two separate phases appear, E, the sample has not dissolved. In the latter case, the capillary is cut at the empty end, another 10 or 20 mm. of solvent are added by means of a capillary pipet, and the process of mixing is repeated. If the droplet appears turbid or two phases persist after the addition of 50 mm. of the solvent, the sample is designated as insoluble in that solvent. The quantity of solvent taken at one time can, of course, be increased or decreased as desired.

In the case of solids, the sample may be introduced into the capillary as in the filling of a melting point tube. The weight of the sample can be determined by weighing on a glass or quartz-fiber balance (Salvioni, 9), torsion spring balance, or the like. About 0.1 mg. should be taken. The solvent is added as with the liquids. Should the solid remain at one end of the capillary after centrifuging instead of passing from one end to another with the liquid, the sample must be stirred with the glass thread as described above.

The comparative specific gravity of the solute and solvent can readily be noted in the case of liquids by observing which is nearest the sealed end of the capillary after centrifuging. The most dense will, of course, be farthest from the center of rotation of the centrifuge.

**SCHLIEREN METHOD.** This method is based on the fact that when even a very small quantity of another substance dissolves in a liquid, the refractive index of that liquid is changed. This change in refractive index can be detected very readily by the *schlieren* phenomenon as described by Emich (8).

In determining the solubility of liquids by this method, the solvent is placed in a *schlieren* cell. (A very good and inexpensive cell is now on the market, obtainable from Microchemical Service, Douglaston, N. Y.) This cell has a capacity of about 0.02 cc. The cell is half filled with the solvent and the solute is added, as in other *schlieren* experiments, from a capillary pipet. With this procedure as with the capillary method, the relative specific gravities of the solute and solvent may be compared, since the stream of solute flowing into the solvent will descend to the bottom of the cell if denser than the solvent or rise to the surface of the solvent if less dense.

The three degrees of solubility are illustrated by the action of ethyl acetate (soluble), 2-methyl butanol (intermediately soluble), and bromobenzene (insoluble) in water. In the first case (ethyl acetate), the solute flowed out freely and immediately dissolved with the formation of pronounced *schlieren*. In the second case (2-methyl butanol), drops formed as the solute left the pipet. These rose to the surface and a few *schlieren* formed. After about three drops had left the pipet, no further *schlieren* were observed. In the last case (bromobenzene), no *schlieren* formed at all and the drops of the liquid settled to the bottom.

In the case of solids, the solute is introduced into the *schlieren* cell by means of a tiny cup at the end of a glass rod (Figure 5). A capillary tube is allowed to collapse at one point in the microflame, and is pushed together at the same time so that a little ball of glass is formed. This is then drawn out while still soft to form a rod about 5 mm. long and turned to form a U. The shorter tube is cut at the point indicated, C, to form the cup, D, which holds about 0.1 to 0.5 mg. of sample. This cup is introduced into the *schlieren* cell as shown in E. The size of the cup must be chosen so that the sample taken fills the cup completely. If, despite this precaution, a small bubble of air remains on top of the cup when it is introduced into the cell, it will be necessary to remove the bubble with a glass thread before the *schlieren* observation can be made. The usual *schlieren* are observed if



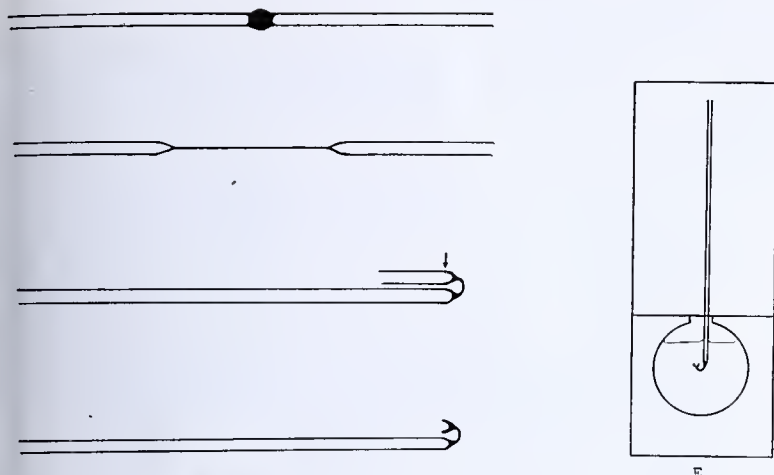


FIGURE 5. SCHLIEREN DETERMINATION OF SOLUBILITY OF SOLIDS

substance is soluble, either ascending or descending; nothing can be observed if the substance is insoluble.

The *schlieren* permit a very sensitive and rapid determination of the solubility of a substance. The authors are working at present with a large number of compounds, both as substances and solvents. The results of this work will be reported in a subsequent paper.

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# Qualitative Separations on a Micro Scale

## Analysis of the Alkali Group

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IN FORMER investigations of this series, an attempt was made to adhere in the transposition to the milligram scale to the procedure of Noyes and Bray (7) as closely as possible. A brief survey of the outline of the authors' scheme which is presented herewith will nevertheless reveal considerable deviations.

The principal change consists in the substitution of chloroplatinic acid for perchloric acid as a reagent for the separation of potassium, rubidium, and cesium from sodium and lithium. The decision on chloroplatinic acid is permissible because of the small quantities of reagents required on the milligram scale. The use of this reagent is preferable from the technical viewpoint, since the chloroplatinates obtained can be easily converted into chlorides by simple ignition.

Additional changes in the analysis of the potassium subgroup consist essentially of a different arrangement of the reagents in which the reagents used by Noyes and Bray are modified. The mixture of the chlorides is first treated with bismuthous acid which enables an immediate detection of cesium if present in quantities larger than 5  $\mu$ g. The immediate isolation of cesium simplifies the remainder of the procedure for the analysis of the potassium subgroup, which now may limit itself essentially to the separation of

potassium and rubidium. The triple chlorides with gold and silver, introduced by Emich as slide tests, are used as confirmatory tests for rubidium and cesium.

As for the working technic, both the tapered (Emich) and the cylindrical (Spikes, 4) microcones are used. Most of the work is performed in Emich cones, and the Spikes cones are used only in the comparison of the volumes of precipitates for the estimation of the quantity of the various metals (3). In part of the work use is made of cones of clear fused quartz. Experience has shown that sodium is always found in blank analyses, when cones of soft or Pyrex glass are used for the ignition of precipitates or residues.

### Procedure (7)

Filtrate F151 from the $(\text{NH}_4)_2\text{CO}_3$ group: + HCl + $\text{BaCl}_2$	BaSO <sub>4</sub> , reject
Filtrate F160: + $(\text{NH}_4)_2\text{CO}_3$	BaCO <sub>3</sub> , reject
Filtrate F161: Evaporate, ignite the residue	NH <sub>3</sub> driven off
Residue R161: + $\text{H}_2\text{PtCl}_6$ + alcohol	
Precipitate P162: Chloroplatinates of K, Rb, and Cs	Extract E162: Chloroplatinates of Na and Li



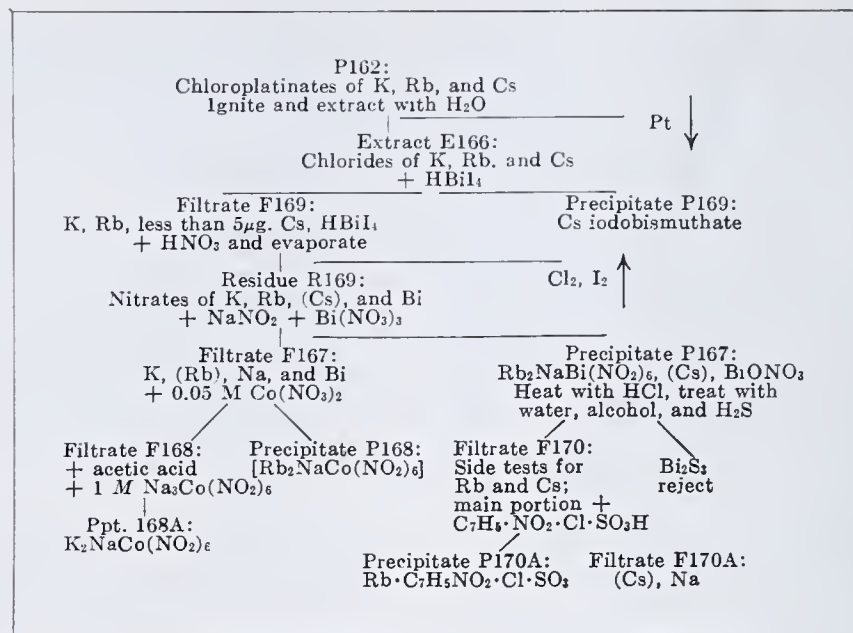
**ELIMINATION OF SULFATE AND AMMONIUM IONS.** Noyes and Bray precipitate the sulfate ion as lead sulfate and remove the excess lead with the use of hydrogen sulfide, a procedure which may have its advantages when working with the customary quantities. On the milligram scale, however, difficulties were experienced in the precipitation of the lead sulfide which showed a tendency to form a rather stable colloidal solution. The removal of the sulfate ion can be performed satisfactorily as described below by precipitation as barium sulfate.

Filtrate F151 from the alkaline earths precipitate is evaporated in an Emich cone to a volume of approximately 20 cu. mm. and then treated with 1-cu. mm. portions of 1 *M* hydrochloric acid until further addition of the acid causes no more effervescence of carbon dioxide. Then sulfate ion is precipitated by the addition of 1 cu. mm. of 0.5 *M* barium chloride solution. Any barium sulfate formed is collected in the point of the cone with the use of the centrifuge, and the supernatant solution is tested for complete precipitation by the addition of another 1-cu. mm. portion of the barium chloride solution. Solution and precipitate are finally separated with the use of centrifuge and capillary pipet. Filtrate F160 is transferred to another Emich cone, the precipitate is washed with two 2-cu. mm. portions of water, and the washings are added to the filtrate. The barium sulfate precipitate is rejected.

Filtrate F160 is treated with 20 cu. mm. of ammonium carbonate reagent prepared by saturating 6 *M* ammonia with solid ammonium carbonate. The mixture is stirred, heated for 5 minutes on the steam bath, centrifuged, and the supernatant solution F161 is transferred to a centrifuge cone of the Emich type made of clear fused quartz. The barium carbonate precipitate is washed once with a 2-cu. mm. portion of the ammonium carbonate reagent, and the washing is added to filtrate F161. The barium carbonate precipitate is rejected.

Filtrate F161 is evaporated to dryness on the steam bath. The residue is ignited for the elimination of the ammonium salts by heating the cone for 2 minutes in a nonluminous Bunsen flame 1 to 2 cm. high. A capillary of approximately 0.5-mm. bore, which is connected to a pressure line (air), is adjusted in a stand at the proper height so as to point downward at an angle of 45 degrees. The cone is held with suitable forceps so that its opening comes close to the opening of the capillary and the stream of air is directed into the interior of the cone. The heating of the cone is started at its point and the flame is brought gradually up to the mouth in order to remove the ammonium salts condensing in the cooler, upper portion of the cone. Air of sufficient pressure is best supplied by a water-blower.

**SEPARATION OF POTASSIUM AND SODIUM SUBGROUPS.** The cone containing the ignited residue R161 is allowed to cool, and the residue is then treated with 10 cu. mm. of a 5 per cent solution of chloroplatinic acid in 13 *M* hydrochloric acid. The mixture is heated on the steam bath for 1 minute with stirring and then evaporated to dryness by blowing a stream of air into the cone while it is being heated on the steam bath. The residue is treated with 20 cu. mm. of 95 per cent ethyl alcohol, and the mixture is thoroughly stirred and then centrifuged. If the supernatant alcoholic solution does not possess a yellow coloration, more chloroplatinic acid must be added. For this purpose the alcohol is first evaporated, the reagent is added, and the treatment with alcohol is repeated after evaporation of the second portion of reagent. The yellow alcoholic extract E162 is finally transferred to another quartz cone, precipitate P162 is washed twice with 3-cu. mm. portions of absolute ethyl alcohol, and the washings are combined with extract E162.



## Analysis of Potassium Subgroup

Utilization of differences in the solubilities of the alkali salts of  $\text{H}_2\text{SnCl}_6$ , tartaric acid, and silicotungstic acid was also tried. None of these reagents proved satisfactory. The procedure given in the accompanying outline was selected, after many trials for its efficiency.

**CONVERSION OF CHLOROPLATINATES OF POTASSIUM SUBGROUP INTO CHLORIDES.** The quartz cone containing precipitate P162 is ignited in a nonluminous

Bunsen flame 1 to 2 cm. high for 2 minutes, as described above for the elimination of ammonium salts. The cone is then allowed to cool, and 20 cu. mm. of distilled water are added to the residue. The extraction of the chlorides is speeded up by stirring the mixture. Finally the metallic platinum is centrifuged to the point of the cone and the clear extract is transferred to a centrifuge cone of the Emich type. The platinum residue is washed twice with 3-cu. mm. portions of water which are combined with extract E166. The platinum may be saved.

**ISOLATION OF THE MAJOR PORTION OF CESIUM.** Extract E166 is evaporated to dryness, and the residue is dissolved by adding 1-cu. mm. portions of distilled water and stirring until a clear solution is obtained. Solution must be accomplished with a minimum of solvent. Then, 10 cu. mm. of  $\text{HBiI}_4$  reagent (5) are added with stirring and the mixture is allowed to stand for 3 minutes at room temperature (0.3 gram of  $\text{Bi}_2\text{O}_3$  is dissolved in 1 ml. of hydriodic acid, specific gravity 1.6, and the solution is diluted with 2 ml. of water). Finally the phases are separated by centrifuging, and the clear solution F169 is transferred to another Emich cone. Precipitate P169 is washed with one 2-cu. mm. portion of the  $\text{HBiI}_4$  reagent, and the washing is combined filtrate F169.

The formation of a red crystalline precipitate of cesium iodobismuthate in this procedure indicates the presence of more than 5  $\mu\text{g.}$  of cesium. With smaller quantities of cesium no precipitate P169 is obtained. The quantity of cesium may be estimated by comparison with iodobismuthate precipitates prepared in a like manner with known quantities of cesium. The formation of the crystalline red precipitate of iodobismuthate in the course of the separation is in itself sufficient proof of the presence of cesium but may be further confirmed by microscopic inspection of the red precipitate.

**SEPARATION OF POTASSIUM FROM THE REST OF THE CESIUM AND FROM THE MAJOR PORTION OF RUBIDIUM.** Filtrate F169 is treated with 5 cu. mm. of 16 *M* nitric acid and heated on the steam bath while a stream of air is passed into the cone to remove the iodine and chlorine liberated. The contents of the cone are finally evaporated to dryness. The residue is treated with 10 cu. mm. of 10 *M* sodium nitrite solution, and the mixture is stirred and finally centrifuged. Occasionally, a white precipitate probably of basic bismuth nitrate is observed at this stage of the analysis. Since such a precipitate does not interfere with the following procedure, it is not separated from the solution. Without regard to the eventual presence of a precipitate 3 cu. mm. of bismuth nitrate reagent (8) are added (6 *M* acetic acid is saturated with bismuth nitrate pentahydrate), the mixture is stirred, and then allowed to stand for 15 minutes at  $0^\circ\text{C}$  (cone immersed in ice water). Any cesium and the major portion of rubidium precipitate. Since no more than 5  $\mu\text{g.}$  of cesium can be present at this stage of the analysis, a large precipitate of yellow crystalline hexanitro-bismuthate indicates the presence of rubidium. If, however, a yellow precipitate fails to appear the "absence" of cesium and of moderate or large quantities (more than 5  $\mu\text{g.}$ ) of rubidium is indicated.

Precipitate and solution are now separated by means of the centrifuge, and the centrifugate is transferred to an Emich cone. Precipitate P167 is washed once with 3 cu. mm. of a mixture of



1 volume of bismuth nitrate reagent and 4 volumes of 9 *M* sodium nitrite. The washing is added to filtrate F167 which must be analyzed immediately, or at least before any appreciable amount of nitrite ion is lost through decomposition.

**ISOLATION OF THE SMALL QUANTITIES OF RUBIDIUM ACCOMPANYING THE POTASSIUM.** Filtrate F167 is treated with 1 cu. mm. of 0.05 *M* cobalt nitrate solution. After mixing with a glass thread, the mixture is allowed to stand in ice water for 15 minutes. Small quantities of rubidium are precipitated together with a small fraction of the potassium present in the solution. However, all the potassium cannot be precipitated at this point, since the potassium-sodium cobaltinitrite is considerably more soluble than the corresponding rubidium salt.

The contents of the cone are centrifuged and centrifugate F168 is transferred to a Spikes cone. Precipitate P168 is reserved without washing to be tested for rubidium in case no rubidium is found in precipitate P167.

**PRECIPITATION AND ESTIMATION OF POTASSIUM.** Filtrate F168 is diluted with an equal volume of 3 *M* acetic acid and then treated with 3 cu. mm. of 1 *M* sodium cobaltinitrite solution. After mixing the contents, the cone is placed in ice water and allowed to remain there for 15 minutes. Any yellow precipitate formed at this time is collected in the point of the cone with the use of the centrifuge. The quantity of potassium is estimated by comparison with potassium-sodium cobaltinitrite precipitates obtained in a like manner from known quantities of potassium.

Simple chemical tests suitable for the recognition of potassium in mixtures with rubidium or cesium are not known. Of course, use could be made of the spectroscope. The identity of potassium may, however, be confirmed in the following way: If the estimation indicates the presence of more than 10  $\mu\text{g.}$  of potassium, its identity is established beyond doubt, as the procedure of separation would under no condition permit more than 5  $\mu\text{g.}$  of rubidium to pass into filtrate F168, and not more than negligible traces of cesium can be present there. Considering the ratio of the atomic weights, 5  $\mu\text{g.}$  of rubidium would give approximately the same volume of precipitate as 2.5  $\mu\text{g.}$  of potassium. If there are more than 10  $\mu\text{g.}$  of potassium estimated, its identity is assured by a margin of safety allowing for large errors in the estimation.

The identity of small quantities of potassium may be confirmed by dissolving the cobaltinitrite precipitate in 2 cu. mm. of 13 *M* hydrochloric acid, testing a droplet of this solution with silver-gold chloride solution as described below, and testing the ignited residue of another droplet with chloroplatinic acid. If the first test reveals the absence of any appreciable quantity of rubidium or cesium, while the second test produces the characteristic crystals of potassium chloroplatinate, the presence of potassium is confirmed.

**ANALYSIS OF PRECIPITATE P167.** The precipitate is treated with 25 cu. mm. of 1 *M* hydrochloric acid, and the mixture is heated on the steam bath until the liberation of oxides of nitrogen ceases. The solution obtained is diluted with 75 cu. mm. of water, and 10 cu. mm. of 95 per cent ethyl alcohol are then added. The mixture, which may contain a precipitate of basic salts of bismuth, is saturated with hydrogen sulfide to convert all the bismuth into the insoluble sulfide. The presence of alcohol in the solution facilitates the collection of the sulfide in the point of the tube with the use of the centrifuge. The clear centrifugate F170 is transferred to an Emich cone and evaporated to dryness on a steam bath. The residue is dissolved in a known volume of 2 or 3 cu. mm. of water. A fraction of a cubic millimeter of this solution is used for a side test.

**SIDE TESTS FOR RUBIDIUM AND CESIUM.** A fraction of a cubic millimeter of the above solution is transferred to a slide and allowed to evaporate. The residue is treated with a droplet of a 1 per cent solution of gold chloride in 13 *M* hydrochloric acid which has been saturated at room temperature with freshly precipitated silver chloride. Blood-red prismatic crystals of  $\text{Rb}_6\text{Ag}_3\text{Au}_3\text{Cl}_{17}$  prove the presence of rubidium (1). The appearance of black cubes or stars of  $\text{Cs}_2\text{AgAuCl}_6$  (1) indicates cesium.

If the unknown contains a large quantity of rubidium, the small quantity of cesium present in filtrate F170 (less than 5  $\mu\text{g.}$ ) usually escapes detection with the above test. Therefore, if a test for cesium is desired, another droplet of a fraction of a cubic millimeter of the concentrated filtrate F170 is transferred to a slide, and an equal volume of  $\text{HbI}_4$  reagent is placed close to this droplet. Contact between the test solution and the reagent is produced by means of a glass thread. Red hexagonal crystals of iodobismuthite show the presence of cesium.

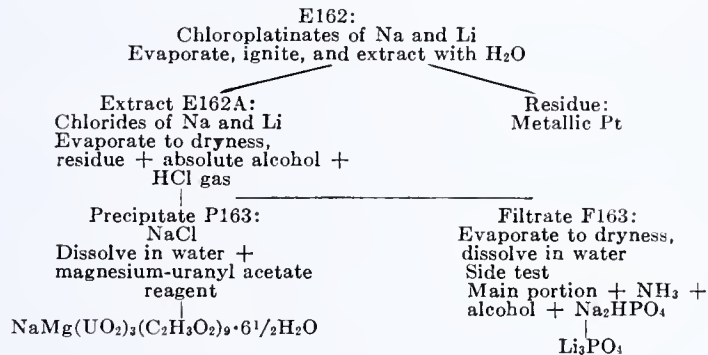
**ISOLATION OF RUBIDIUM AND ESTIMATION OF ITS QUANTITY.** The remainder of the concentrated filtrate F170 is treated with an equal volume of saturated solution of sodium 6-chloro-5-nitrotoluenesulfonate, mixed, and cooled in ice water for 10 minutes. Rubidium precipitates as a white crystalline salt of

the sulfonic acid. For the estimation of the quantity of rubidium, the precipitate is compared with precipitates obtained in a like manner with known quantities of rubidium. A correction must be applied to account for that part of filtrate F170 used in the side tests.

Filtrate F170A from the sulfonate precipitate could be used for a further search for cesium, just as precipitate P170A could be used for the confirmation of rubidium. It is, however, more convenient to perform these confirmatory tests before the addition of sulfonate reagent.

**TEST FOR RUBIDIUM IN PRECIPITATE P168.** If less than 5  $\mu\text{g.}$  of rubidium are present in the unknown, the rubidium will not be found in filtrate F170. To test for the presence of a small quantity of rubidium in precipitate P168, the precipitate is dissolved in 2 cu. mm. of 13 *M* hydrochloric acid, and the solution is transferred to a slide and tested with the silver-gold chloride reagent of Emich (1).

### Analysis of the Sodium Subgroup



**CONVERSION OF THE CHLOROPLATINATES OF THE SODIUM SUBGROUP INTO CHLORIDES.** Alcohol extract E162 is evaporated at room temperature by blowing a stream of air over the surface of the solution. Heating is not permissible since it causes severe bumping and loss of solution. The residue is ignited by holding the cone directly in a nonluminous Bunsen flame as described above. After ignition for at least 1 minute, the cone is allowed to cool, the residue is extracted with 10 cu. mm. of water, and the extract is transferred to a Pyrex cone of the Emich type. The residue of metallic platinum is washed twice with 3-cu. mm. portions of water, and the washings are combined with extract E162A. The metallic platinum may be saved, although its value will hardly exceed \$0.01.

**SEPARATION OF SODIUM AND LITHIUM.** Extract E162A is evaporated on a steam bath. The dry residue is treated with 20 cu. mm. of absolute alcohol which has been saturated with dry hydrogen chloride gas. The mixture is stirred and then allowed to stand for 30 minutes in an atmosphere of dry hydrogen chloride (4). After centrifuging, the clear solution is transferred to a Spikes cone and the residue is washed with two 2-cu. mm. portions of the alcoholic hydrogen chloride. The washings are combined with the centrifugate.

**CONFIRMATORY TEST FOR SODIUM AND ESTIMATION OF ITS QUANTITY.** The precipitated sodium chloride P163 is dissolved by adding 1-cu. mm. portions of water and stirring until solution is complete. A minimum of solvent should be employed. The solution is treated with an equal volume of magnesium-uranyl acetate reagent (8), and after mixing is allowed to stand for 5 minutes at 0° C. (Ten grams of uranyl acetate dihydrate, 33 grams of magnesium acetate tetrahydrate, and 12 grams of 99.5 per cent acetic acid are dissolved in water to make 100 ml. of solution. After standing for 2 days, the solution is filtered.) Formation of a greenish yellow precipitate proves the presence of sodium. Its quantity is estimated by comparison with precipitates obtained in a like manner with known quantities of sodium.

Microscopic inspection of the triple acetate and the flame test may be used for the additional confirmation of the presence of sodium.

**CONFIRMATORY TEST FOR LITHIUM.** Filtrate F163 is evaporated to dryness on a steam bath. The residue is dissolved in a minimum of solvent by adding 1-cu. mm. portions of water and stirring until solution is complete. A fraction of a cubic millimeter of this solution is transferred to a slide. An equal volume of zinc-uranyl acetate reagent (6) is deposited on the slide at a distance of approximately 1 mm. from the droplet to be tested [(1) 10 grams of uranyl acetate dihydrate are dissolved in 6 grams of 30 per cent acetic acid and 49 ml. of water; (2) 30 grams of zinc acetate trihydrate are dissolved in 3 grams of 30 per cent acetic acid and 32 ml. water. (1) and (2) are mixed, and the mixture is



TABLE I. QUANTITY OF ALKALI GIVING VISIBLE PRECIPITATE

Reagent	Smallest Quantity of Alkali Giving a Precipitate Visible in the Microcone				
	K μg.	Rb μg.	Cs μg.	Na μg.	Li μg.
H <sub>2</sub> PtCl <sub>6</sub>	2	2	1	...	...
HBiI <sub>4</sub>	...	...	4	...	...
NaNO <sub>2</sub> + Bi(NO <sub>3</sub> ) <sub>3</sub>	...	2	2	...	...
Na <sub>3</sub> Co(NO <sub>2</sub> ) <sub>6</sub>	0.5	0.3	...	...	...
Na <sub>2</sub> SO <sub>3</sub> ·C <sub>6</sub> H <sub>5</sub> ·CH <sub>3</sub> ·NO <sub>2</sub> ·Cl	...	6	...	...	...
HCl + alcohol	...	...	...	5	...
Mg-UO <sub>2</sub> acetate	...	...	...	2	...
Na <sub>2</sub> HPO <sub>4</sub>	...	...	...	...	5
Limits of Identification of Slide Tests					
H <sub>2</sub> PtCl <sub>6</sub>	0.03	0.03	0.02	...	...
AgCl-AuCl <sub>3</sub> reagent (1)	...	0.1	0.1	...	...
HBiI <sub>4</sub>	...	...	0.02	...	...
Mg-UO <sub>2</sub> acetate	...	...	...	0.4 <sup>2</sup>	0.5
Zn-UO <sub>2</sub> acetate	...	...	...	0.4	0.3

filtered after 24 hours]. The droplets are drawn together by means of a glass thread. The crystals of lithium-zinc-uranyl acetate have a circular outline and are easily distinguished from the otherwise similar crystals of the corresponding sodium compound which possess an oblong outline.

**ESTIMATION OF THE QUANTITY OF LITHIUM.** The main portion of the concentrated lithium chloride solution is evaporated to dryness, and the residue is taken up in 5 cu. mm. of 15 *M* ammonia. This solution is treated with 5 cu. mm. of 95 per cent ethyl alcohol, stirred, centrifuged, and separated from any precipitate which may have collected in the point of the tube. The clear ammoniacal solution is treated in a Spikes cone with a 5 per cent Na<sub>2</sub>HPO<sub>4</sub> solution which is added in 1-cu. mm. portions until no further precipitation is produced. The mixture is stirred after addition of each portion of the reagent, then centrifuged, and the next portion of reagent is added to the clear supernatant solution. An excess of the reagent must be avoided, as lithium phosphate is slightly soluble in the reagent. The volume of the phosphate precipitate is finally compared with the volumes of lithium phosphate precipitates obtained likewise with known quantities of lithium.

A flame test with the phosphate precipitate may serve for additional confirmation of the presence of lithium.

### Limitations of the Scheme

The proposed scheme permits the detection of 10 μg. of any of the alkalis in mixtures with 500 μg. of any other alkali. Complete recovery must not be expected, however, as the noticeable solubility of the precipitates renders the separations incomplete—for example, in the analysis of a mixture containing 500 μg. of potassium, 10 μg. of cesium, and 10 μg. of sodium, the following quantities were recovered: 400 μg. of potassium, 5 μg. of cesium, and 5 μg. of sodium. The estimation of the large quantity of potassium is rather unreliable and does not confirm the loss of 20 per cent of the potassium.

Table I records the smallest quantities of the alkalis which, with the reagents listed, give visible precipitates in microcones under the conditions prescribed. The reagents are listed in the order in which they are employed in the analysis. Table I shows that less than 2 or 1 μg. of potassium, rubidium, and cesium go into the filtrate of the sodium subgroup; less than 4 μg. of cesium escape precipitation with the HBiI<sub>4</sub> reagent; less than 2 μg. of cesium and rubidium are not precipitated by sodium nitrite and bismuth nitrate and go into the filtrate containing the potassium. Less than 5 μg. of sodium and lithium escape precipitation as sodium chloride and lithium phosphate, respectively.

The limits of identification of the slide tests make it possible to test for small quantities of potassium, rubidium, cesium in filtrates of the sodium subgroup, and to test for sodium in the filtrate which is supposed to contain the lithium.

### Summary

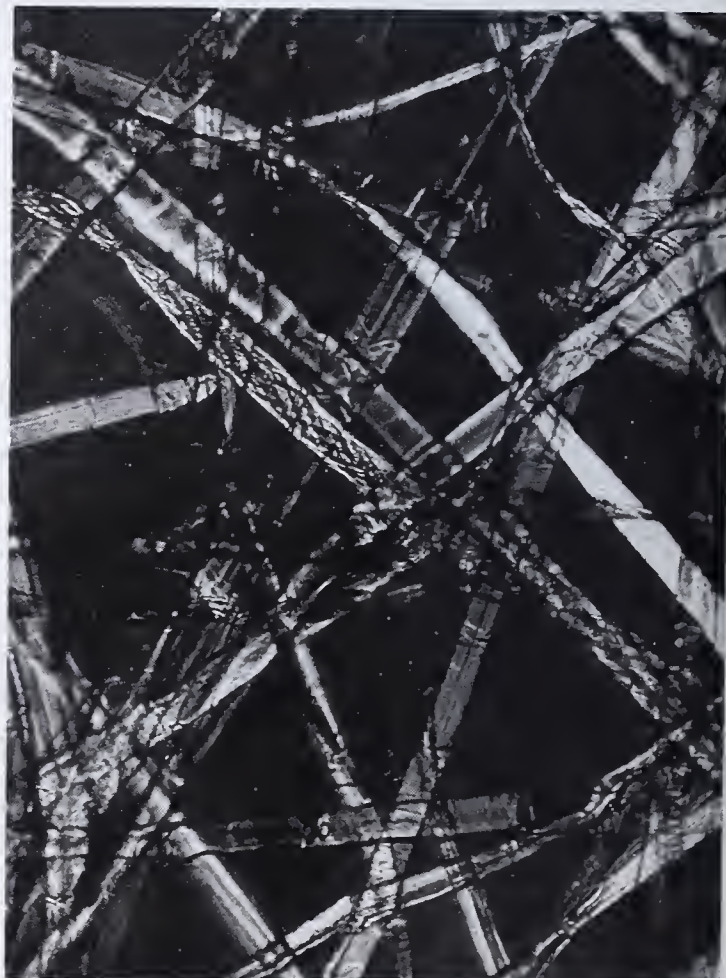
A procedure is proposed for the qualitative analysis of the alkali group from 1-mg. solid samples. The scheme provides

for the detection and estimation of 10 μg. of any alkali metal in mixtures containing up to 500 μg. of other alkalis. Sulfate ion is removed as barium sulfate. Chloroplatinic acid is used for the separation of the potassium and sodium subgroups. The analysis of the sodium subgroup follows the scheme of Noyes and Bray. In the analysis of the potassium subgroup the scheme of these authors is modified by using the reagents in a different order. The work is carried out in microcentrifuge cones of clear fused quartz and of Pyrex glass.

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- (7) Noyes, A. A., and Bray, W. C., "Qualitative Analysis for the Rare Elements," New York, Macmillan Co., 1927. (The paragraph numbers of this text have been used as a guide in numbering the filtrates and precipitates mentioned in this article.)
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RECEIVED December 21, 1937. Presented in preliminary form before the Microchemical Section at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937.



Courtesy, J. R. Rachele  
and J. T. Bryant

LENS PAPER IN POLARIZED LIGHT



# Microdetermination of Halogen by Combustion

## An Absorption Apparatus

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THE regular Pregl method for the determination of halogen and sulfur consists in burning the sample in a combustion tube with oxygen and passing the combustion gases over a spiral which is placed in the end of the tube and is moistened with a suitable absorbing solution. When the sample has been burned, the tube is allowed to cool, the absorbed products are rinsed out with distilled water, and the tube is washed with acetone and then dried by the passage of a stream of air. Cooling, rinsing, and drying require 5 to 7 minutes each, and where routine determinations are carried on day after day, this expenditure of time is appreciable.

While the amount of actual working time during the combustion was reduced by the introduction of the electric furnace for automatic combustion (1), the total working time was reduced to a desirable minimum by a new design of the absorption part of the tube which facilitates the introduction and removal of the absorbing solution, permits the products absorbed to be removed immediately after combustion, and eliminates the necessity for drying the combustion tube afterwards. Thus, the total time required for the performance of a halogen determination was shortened by 10 to 15 minutes.

### Apparatus

The absorption apparatus consists of a clear fused-quartz tube sealed on to the combustion tube, *A* (Figure 1). One to 2 ml. of the absorbing solution are added by means of a pipet, the point of which is inserted through the funnel, *C*, and brought down to a level approximately 5 mm. above the filling of the small chamber, *E*. This prevents creeping or spattering of the absorbing solution into tube *A* and its failure to be removed when the absorbing products are rinsed into the receiver. The glass stopper, *B*, is then inserted and sealed by introducing a few drops of water into the funnel, *C*. The stopcock at the outlet of the absorption tube is, of course, kept closed during the introduction of the absorbent as well as during the combustion. The flow of gas through the apparatus causes the absorbing solution to rise around the helix and keep it moist at all times.

The combustion gases enter the small absorption chamber, *E*, which is filled with short pieces of curved Pyrex glass rod or with Pyrex glass beads 3 to 4 mm. in diameter. The short pieces of glass rod are obtained by cutting a helix of the dimensions as used in the absorption tube into pieces 1 cm. long and fire-polishing the sharp edges. On leaving *E*, the combustion gases are led down through the narrow tube, *F*, ascend along the glass helix, and leave through the by-pass, *D*, and the funnel, *C*.

To collect the absorbed products in a flask or beaker, the stopcock must

first be opened. The stopper, *B*, is loosened from its seat without actually removing it from the funnel, and 30 ml. of distilled water are poured in 5-ml. portions into the funnel. What fraction of the wash liquid will flow into by-pass *D* and down the section of the tube containing the helix is determined by the rate of addition of the water. The entrance to chamber *E* may be partly closed with stopper *B* and more of the wash water will thus be deflected into the by-pass. As a general rule both sections of the absorption tube—i. e., chamber *E* and the helix—should be completely and simultaneously rinsed.

The absorption tube just described was designed especially for the absorption of iodine. The iodine is mainly absorbed on the glass filling of *E* which is moistened with sodium carbonate solution. This part of the apparatus is kept warm enough by the heat from the furnace so that all of the iodine sublimes into the sodium carbonate and is absorbed. Gaseous products, such as hydrogen chloride and hydrogen bromide, are also completely absorbed on the way along the glass helix. Although the apparatus was designed primarily for halogens, it may be used for the absorption of other gases by using suitable solutions.

For reasons of economy, a glass rather than a quartz stopcock was used at the outlet of the absorption tube and was attached by means of a tubing of pure rubber. The whole absorption tube could be made of hard glass and a ground joint might be used for the connection to the quartz combustion tube. However, this is not recommended for the absorption of the iodine, because the outlet of the combustion tube and the inlet of the absorption apparatus must be kept fairly warm. Freezing of the joint is likely to occur and the warm part of the glass apparatus is liable to crack if wash water is spilled on it. On the other hand, with an apparatus made completely of quartz, it is a relatively simple matter to cut off the absorber and to seal it to another combustion tube whenever necessary.

### Literature Cited

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RECEIVED November 22, 1937. Communication 653 from the Kodak Research Laboratories. The apparatus was briefly described before the Microchemical Section at the 94th Meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937, in connection with the paper "An Electric Organic Combustion Furnace for the Automatic Burning of the Sample."

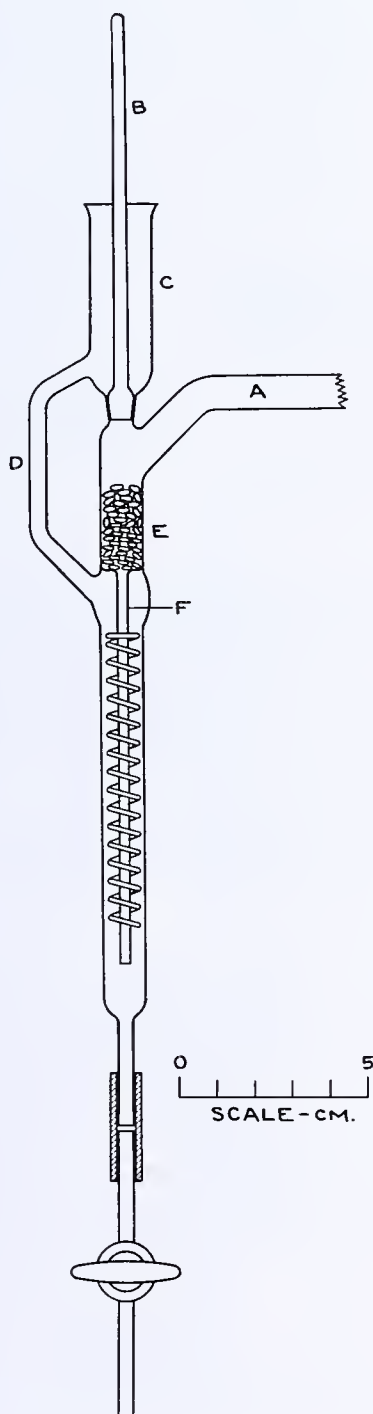


FIGURE 1. APPARATUS



# The Microdetermination of Calcium

G. H. ELLIS, Laboratory of Animal Nutrition, Cornell University, Ithaca, N. Y.

DURING the course of a biological investigation, the need arose to determine calcium in certain tissues of the rat. In many instances, the amount of tissue available necessitated a method requiring not more than 5 or 10 gamma of calcium per determination.

The technic of Miller and Kirk (3), based on the oxalate-permanganate volumetric method, was tried, but was discarded because of the difficulty in determining the end point in the titration. Lindner and Kirk (2) later surmounted the difficulties encountered in the earlier method by replacing potassium permanganate with ceric sulfate, which is added in excess to the calcium oxalate precipitate dissolved in dilute sulfuric acid. The ceric sulfate not reduced by the oxalate is then determined by titration with standard ferrous ammonium sulfate, using phenanthroline-ferrous sulfate as an indicator.

TABLE I. COMPARISON OF MACRO- AND MICROMETHODS

Volume of Sample	Calcium Present	Volume of 0.01 N Cerate Solution	Calcium Found	Deviation from Amount Present
$\lambda$	$\gamma$	$\lambda$	$\gamma$	%
51.9	7.37	36.0	7.20	-2.3
		37.0	7.40	+0.4
		36.6	7.32	-0.7
		37.6	7.52	+2.0
		37.3	7.46	+1.2
		36.4	7.28	-1.2
		36.6	7.32	-0.7
		Mean	7.36	

This method proved very satisfactory. A somewhat simpler procedure is afforded by the use of hexanitrate ammonium cerate (obtainable from the G. Frederick Smith Chemical Company, Columbus, Ohio), which was suggested by G. Frederick Smith, of the University of Illinois. The cerate solution is relatively stable. A 0.01 N solution in 1 N perchloric acid stored in clear glass at room temperature lost 3 per cent in strength over a period of 4 months. In the titra-

tion of oxalate ion the end point is sharp, and the titration can be carried out at room temperature.

The technic of the calcium determination is essentially that of Lindner and Kirk, with the exception of the titration of the calcium oxalate, which is dissolved in about 1 ml. of a 3.5 per cent solution of perchloric acid and titrated with a 0.01 N solution of hexanitrate ammonium cerate which is 1 N with perchloric acid. Orthophenanthroline ferrous complex (0.0005 M) or setopaline C (1 per cent aqueous solution) is a satisfactory indicator, particularly the latter, since it uses up practically no cerate solution.

When calcium is precipitated in the presence of proteins the calcium oxalate crystals are very small and, in spite of long digestion losses of the precipitate through the filter stick used by Miller and Kirk, are practically unavoidable. To overcome this difficulty, the precipitate was separated by centrifuging. The precipitation was carried out in pointed tubes of 1- or 2-ml. capacity. After standing for an hour or more the tubes were centrifuged, the supernatant liquid was drawn off by means of a long-tipped medicine dropper, and the precipitate was washed once or twice with ammonium hydroxide solution (1 to 9) saturated with calcium oxalate. The washed precipitate was then dissolved as above, transferred to a 1- or 2-ml. beaker, and titrated. When the material is ashed as recommended by Lindner and Kirk, either filtration or centrifugation may be used for the isolation of the precipitate of calcium oxalate.

Table I gives a comparison of the micromethod with the macromethod of Kramer and Howland (1). The calcium present in a solution of bone salts was determined by the macromethod, and after suitable dilution samples were taken for microanalysis.

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RECEIVED September 25, 1937. Study supported by funds from the Rockefeller Foundation Grant for Research in Longevity.

## Fume Tube for Micro-Kjeldahl Digestions

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IT OFTEN happens that hood space is not conveniently available in which to carry out micro-Kjeldahl digestions. For use in such cases, fume tubes (Figure 1, upper) are on the market. These are supposed to carry the acid fumes to an ordinary water-aspirator, but in this laboratory the capacity of a water-aspirator has been found to be entirely inadequate and a fume tube of this sort is almost valueless.

Figure 1 (lower) illustrates a very satisfactory air-aspirator built in this laboratory. Compressed air is led in as indicated and proceeds through the narrow aperture at A, aspirating the fumes into the exit tube. In the author's practice the exit tube leads to the open air through a hole cut in a window casing. The fume tube as a whole is clamped in a slightly sloping position, so that whatever liquid condenses therein will flow out at the exit, where it is caught in a dish set on the window shelf.

The capacity of such an air-aspirator is very large. In addition to a four-hole tube as illustrated, a twelve-hole tube is in use, with the aspirator leading through a tee with six holes on each side. An aspirator of the dimensions indicated has ample capacity even in this case.

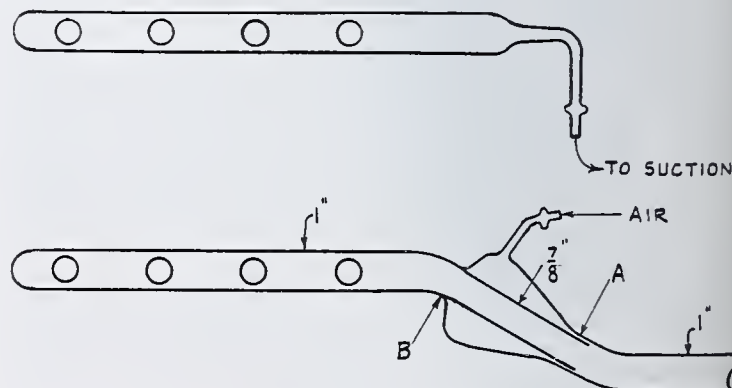


FIGURE 1. FUME TUBES

The apparatus is made of Pyrex and the glass-blowing is not particularly difficult. However, the double seal at B might be replaced by a rubber stopper if desired, since the apparatus at this point is not subjected to the action of either fumes or condensate.

RECEIVED January 10, 1938.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## The Ultracentrifuge and Its Field of Research

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**C**OLLOIDS and high-molecular substances are the building stones of the cells and the various tissues of the organisms. Life is not possible without these substances, because no other material lends itself to the manifold performances here required. No other material offers such a wealth of varieties, such pliable forms. Accordingly the biological and medical sciences which aim at an elucidation of the processes taking place in living beings are interested in the properties of high-molecular substances. Only by a detailed study of the behavior of these compounds will it be possible to find proper remedies in the case of disturbances. It is obvious, therefore, that our bodily welfare is highly dependent on our knowledge of the properties of the macromolecules of high-molecular compounds. Illness and death cannot be fought successfully if we do not know the chemistry and physics of the high-molecular material of our own body.

When human beings began to improve their conditions by making weapons, various domestic appliances, and clothing they had to borrow from animals and plants to supplement what their own bodies lacked. Clubs of wood were used as substitutes for the heavy paw of the lion and the bear, the hide of a cow or sheep was swept around the body to protect the thin human skin. Thus was laid the foundation for the creation of the superbeing which modern man together with all his technical facilities represents. The human faculties were extended until nowadays man is a brain in the center of a superbody.

The craftsman of old times had to use what his low creatures, the animals and plants, made. In our days powerful industries are busy producing artificial substitutes for many of the natural materials. Paper makes papyrus and aluminum superfluous, artificial silk makes it unnecessary to cultivate the silkworm, synthetic rubber makes us inde-

pendent of the rubber plants, etc. Not only substitutes but entirely new products, such as cellulose derivatives, artificial resins, and other synthetic polymerization products are finding extensive use in the service of modern man. In all these cases we are dealing with high-molecular substances and colloids. It does not take deep thinking to conclude that many indispensable articles of our daily life would be unsuitable and too expensive, if we did not know the right way to produce them, and this, in its turn, requires knowledge of high-molecular compounds.

Three hundred years ago the first Swedish settlers tried to find their living on the shores of the Delaware, using very simple utensils and obtaining the necessary products from the cultivation of plants and animals. In our days the same place is the site of powerful industries producing in a better and cheaper way many of the necessities of daily life.

### Development of the Ultracentrifuge

The realization of the important role played by high-molecular compounds both in the life of the organisms and in many industrial processes has awakened a lively interest in systems of this kind and a number of new methods are being applied in their study. One of the new tools is the ultracentrifuge.

Before describing the present forms a few historical notes may be permitted. The ultracentrifuge originated in some work on colloids done in Upsala about 1920 concerning particle size in gold sols (68). We had tried to determine distribution

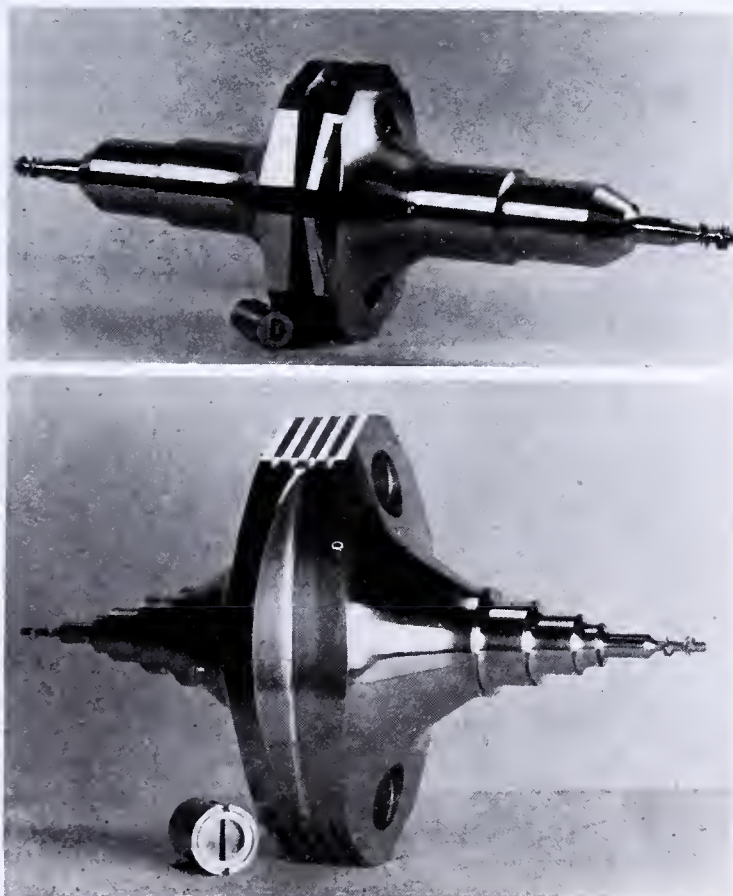


FIGURE 1. ROTORS AND CELLS

Upper. For centrifugal fields up to 710,000 times the force of gravity. Largest diameter, 10.4 cm.; mean active radius, 3.25 cm.; height of column of solution, 0.8 cm. Lower. For centrifugal fields up to 300,000 times the force of gravity. Largest diameter, 18 cm.; mean active radius, 6.5 cm.; height of column of solution, 1.8 cm.



curves by recording the settling of the particles under the influence of gravity. Only very coarse-grained sols (down to about  $100\text{ m}\mu$ ) could, however, be studied in that way. It was natural for me to turn my attention to the possibility of increasing the force acting upon the particles by using a centrifugal field instead of the field of gravity. Earlier attempts in this direction had not been very successful, however, and when I spoke to my research students about this possibility they were not very enthusiastic about it. It was not until I came to the University of Wisconsin as a visiting professor in 1923 that I found interest in this problem. J. B. Nichols, now at the du Pont Experimental Station in Wilmington, was willing to cooperate with me. We built a small machine allowing optical observations of sedimentation to be carried out during rotation (67).

The field was not more than about 1000 times gravity and sedimentation could be followed only for a short period, owing to convection currents. We felt confident, however, that the problem could be solved.

After my return to Upsala, Dr. Rinde and myself undertook a systematic study of the conditions of convection-free sedimentation, using fine-grained gold sols as test objects (69). In the first place, we found that the sample of solution studied must be sector-shaped in order to permit the molecules to travel along radii and not strike against the walls of the vessel enclosing the sample. Secondly, the temperature of the column of liquid has to be kept constant both in space and time; otherwise convection currents caused by density differences set in. We therefore spun our first rotors in hydrogen at atmospheric pressure so as to reduce materially the heat caused by friction against the surrounding gas.

In 1924 we were able to perform faultless sedimentation in centrifugal fields 5000 times the force of gravity and to measure the size distribution in gold sols down to the most fine-grained ones. The name ultracentrifuge was proposed for this new research tool. Using the same apparatus Fåhræus and I (1925) succeeded in determining the particle weight of hemoglobin by means of sedimentation measurements (64).

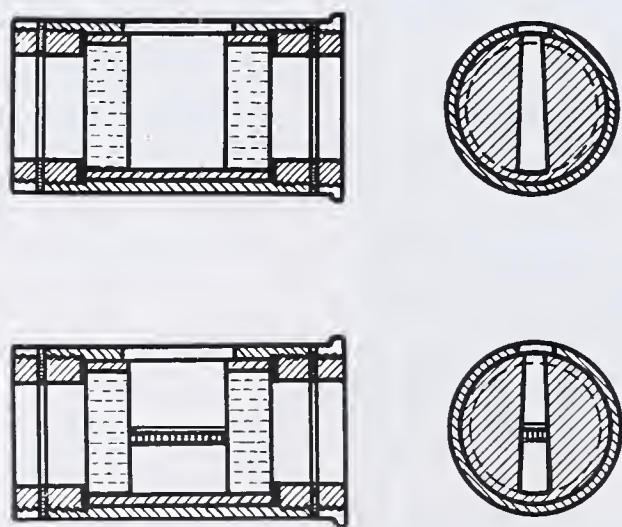


FIGURE 3. SECTION OF CELLS

Upper. Cell for optical observations  
Lower. Cell for separation under optical control

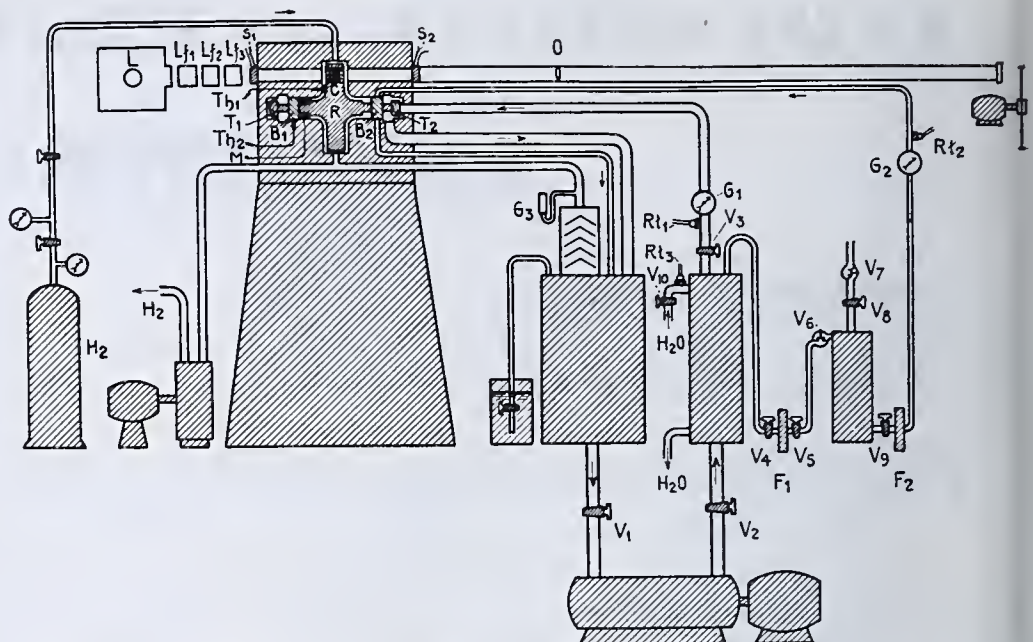


FIGURE 2. DIAGRAMMATIC REPRESENTATION OF OIL-TURBINE ULTRACENTRIFUGE

Contrary to expectations, we found that the solution of this protein is monodisperse and defined by the environment. One is therefore justified in speaking about its particle mass as its molecular weight. This finding stimulated interest and one of the medical foundations in Sweden (Therese och Johan Anderssons Minne) granted me a sum of money sufficient for building a high-speed ultracentrifuge to study the behavior of protein molecules in intense centrifugal fields. Collaboration with Ljungström and Lysholm enabled me to obtain convection-free sedimentation in fields 100,000 times gravity in 1926 (66). In the spring of 1931 further improvements of the machinery accomplished by Boestad and me made possible sedimentation measurements at 200,000 times gravity (mean radius  $x = 65\text{ mm.}$ ; height of column of solution =  $12\text{ mm.}$ ;  $54,000\text{ r. p. m.}$ , 51). Using the same radius and the same height of column of solution, we reached 260,000 times gravity early in 1932 (61), 300,000 in the spring of 1932 (56), and 400,000 in the spring of 1933 (49, 52, 57).

Essentially higher fields cannot be utilized with rotors of this size because of failure of the material. It seemed of interest to try a smaller rotor type capable of giving considerably higher intensities although at the sacrifice of height of column of solution and homogeneity of the centrifugal field. Reducing the mean radius from 65 to 36 mm. and the height of sample from 18 to 8 mm., sedimentation measurements in fields up to 600,000 times gravity were made in the fall of 1933 (55) and up to 900,000 times gravity in the summer of 1934 (48, 60). The rotors used in these experiments exploded, however, after a few runs. A further reduction of the mean radius to 32.5 mm. and improvements in the construction have made it possible to do regular measurements in fields up to 710,000 times gravity (32). The comparison of measurements made in very intense centrifugal fields, using a low column of solution and a small mean radius, with measurements made in somewhat less intense fields using a higher sample situated farther from the center of rotation has shown that the accuracy is much better in the latter case, at least as far as sedimentation velocity measurements are concerned.

Theoretical considerations (O. Quensel and K. O. Pedersen) and experimental tests have shown that the power of the ultracentrifuge to resolve a mixture of molecular species is proportional to  $\omega^2 x h$ , where  $\omega$  is the angular velocity,  $x$  the distance from the center of rotation, and  $h$  the height of column of solution (54). The largest value for this product reached so far is  $5.83 \times 10^8$  (70,000 r. p. m.,  $h = 1.65\text{ cm.}$ ,



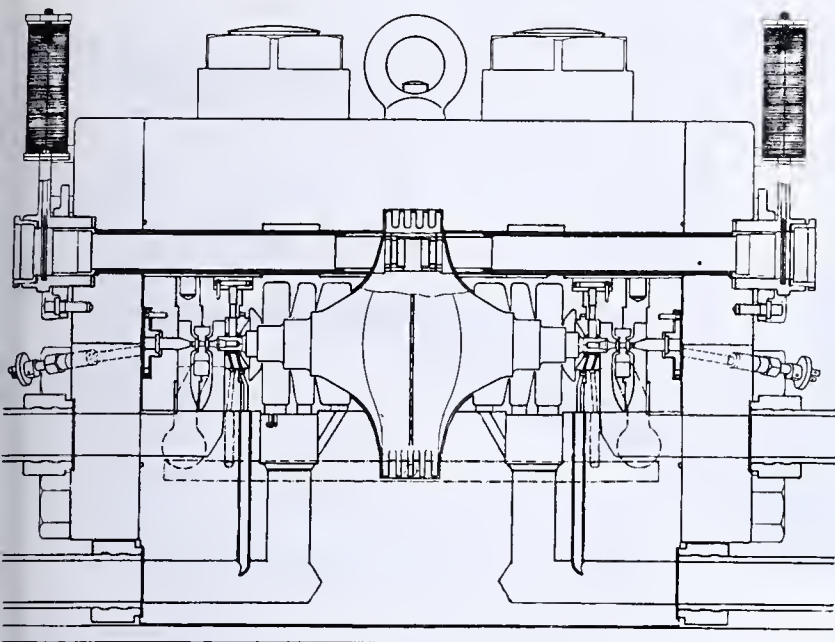


FIGURE 4. AXIAL SECTION OF OIL-TURBINE ULTRACENTRIFUGE

= 6.58 cm.). For standard equipment, therefore, a large rotor is to be preferred.

From the many different experimental machines built in Upsala, two standard types have been developed (48). The first is adapted for the region 500 to 15,000, and the other for the range 15,000 to 750,000 times gravity. The low-speed machine is driven directly by a high-frequency motor and is provided with ball bearings. The rotation takes place in hydrogen at atmospheric pressure and the casing is immersed in a water thermostat. It is used for sedimentation equilibrium measurements in solutions of high-molecular substances and for sedimentation velocity measurements on heavy particles.

Our high-speed machine is driven by oil turbines and has white-metal bearings with movable, damped pistons. The rotor spins in hydrogen at reduced pressure. It is used for velocity measurements in solutions of high-molecular compounds and for equilibrium measurements on low-molecular substances.

A few details concerning the oil-turbine ultracentrifuge may be of interest. The sample to be studied is enclosed in a sector-shaped cell provided with plane-parallel quartz windows (Figures 1 and 3). Recently a cell type with a dividing membrane in the middle has been introduced for analytical termination of sedimentation.

The rotor (Figures 1 and 2) of chromium-nickel steel is supported on horizontal bearings,  $B_1$  and  $B_2$ , and kept in rotation by means of two small twin-oil turbines,  $T_1$  and  $T_2$ , one on each end of the shaft. Hydrogen is admitted at the periphery and constantly pumped off so as to maintain a pressure of about 20 mm. Thermocouples are in the bearings and a radia-

tion thermocouple,  $Th_1$ , near the rotor serve for temperature control of the centrifuge. A beam of light from a mercury lamp,  $L$ , filtered through  $Lf_1$ ,  $Lf_2$ , and  $Lf_3$ , passes the cell,  $C$ , in the rotor on its way to the camera. The exposures are timed by means of the electromagnetic shutters,  $S_1$  and  $S_2$ . For speed measurements and speed control a magnetic generator,  $M$ , is used in connection with a reed-frequency meter, an oscillograph, or a frequency bridge.

The pressure oil which feeds the turbines is produced by a special oil compressor, cooled and thermostated to a suitable temperature before entering the turbine chambers. A system of channels in the heavy steel casing makes it possible to thermostate the centrifuge by means of oil or water circulation. The lubrication oil for the bearings passes through an oil filter and is controlled by valve  $V_3$ . By changing the speed of the motor which drives the compressor and by operating valve  $V_3$ , the pressure of the oil entering the turbines may be regulated so as to make possible sedimentation measurements at any desired speed between 5000 and 140,000 r. p. m. The resistance thermometers,  $Rt_1$ ,  $Rt_2$ , and  $Rt_3$ , and the manometers,  $G_1$ ,  $G_2$ , and  $G_3$ , enable the operator to control temperature and pressure in various parts of the machinery.

A detailed section of the centrifuge proper through the axis of rotation is given in Figure 4.

Figure 5 gives a view of the installation showing the camera, the centrifuge on its foundation, the oil coolers, and the hand rails leading to the pit where the motor, compressor, and filters are located.

Recently an air-turbine-driven, self-balancing ultracentrifuge has been developed by Beams (5) of the University of Virginia and improved and adapted to sedimentation measurements by Bauer (4) and by Wyckoff (7) at the Rockefeller Institute in New York. Here a light Duralumin rotor hangs

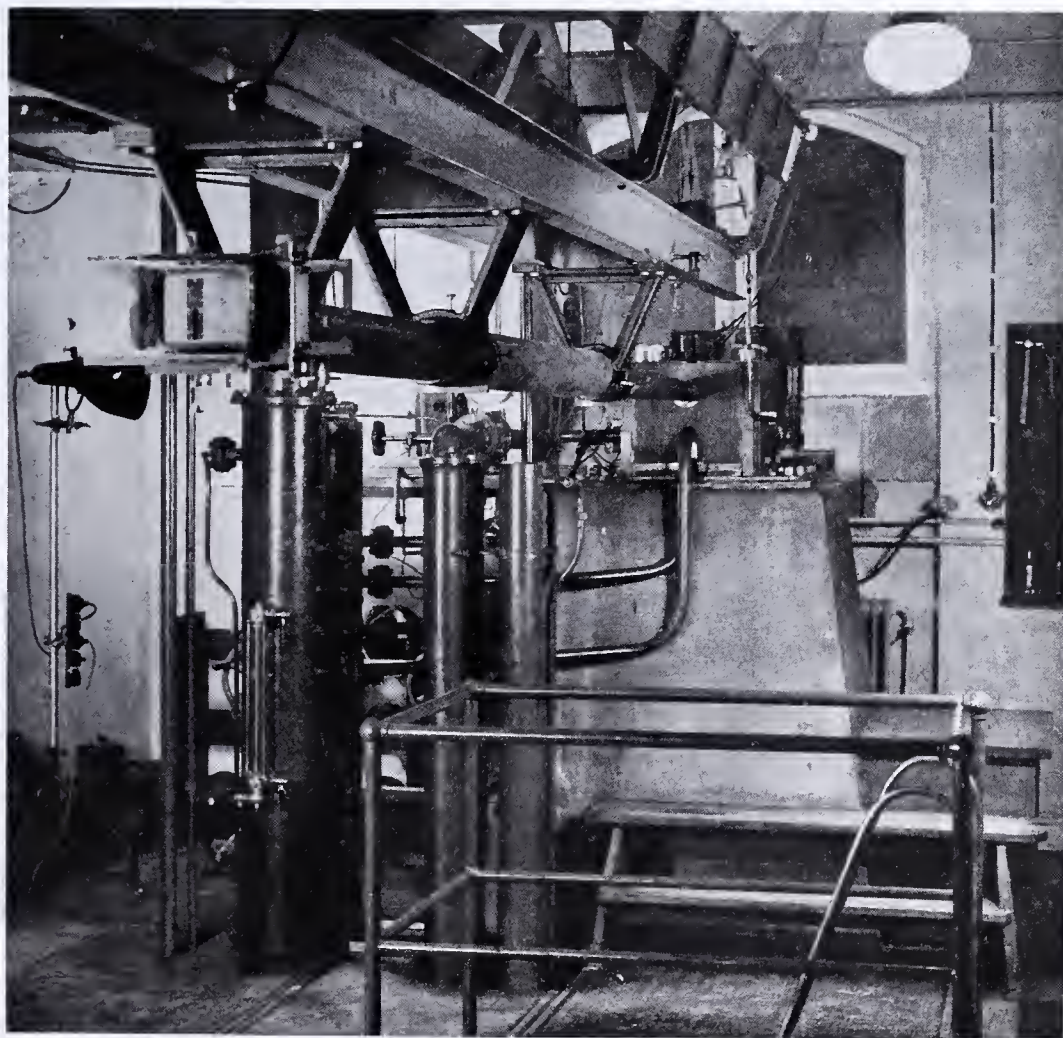
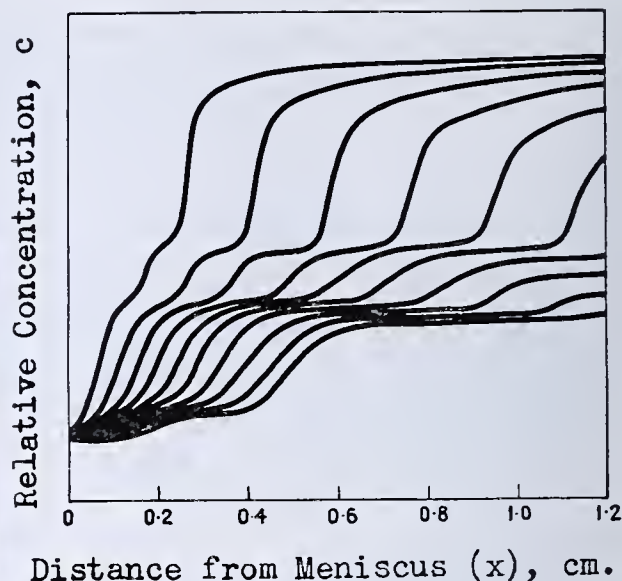


FIGURE 5. OIL-TURBINE ULTRACENTRIFUGE INSTALLATION



FIGURE 6. SEDIMENTATION PICTURES OBTAINED BY LIGHT-ABSORPTION METHOD (LEFT) AND CURVES OF CONCENTRATION DISTRIBUTION FOR LIMULUS HEMOCYANIN AT pH 6.8 (RIGHT) (ERIKSSON-QUENSEL)

Sedimentation constants of components,  $56.5 \times 10^{-13}$ ,  $34.6 \times 10^{-13}$ ,  $16.1 \times 10^{-13}$ , and  $5.9 \times 10^{-13}$ . Centrifugal force 120,000 times gravity. Time between exposures, 5 minutes



on a thin steel shaft and is supported by an air-film bearing. The friction, and consequently the energy consumption, are therefore very low. The air turbine is sealed off from the vacuum chamber in which the rotor moves by surrounding the vertical shaft with an oil-gland-shaped bearing. Beams has further succeeded in spinning electrically a hanging Duralumin rotor supported by an air-film bearing (6). These new types of ultracentrifuge promise to be of great service in many cases, although the resolving power has not yet been pushed to the height obtainable with the steel rotor of the oil-turbine ultracentrifuge.

### Sedimentation

The process of sedimentation is in most cases followed by optical means. Two different properties of the solute may be utilized for the determination of the concentration distribution in the rotating solution—namely, the light absorption and the refraction. In both cases the thickness of the layer of liquid studied necessitates long-focus lenses in order to avoid parallax errors. When using the absorption method, photographic exposures of the sedimenting column are made from time to time by light of a wave length absorbed by the solute. These pictures are then measured by means of a microphotometer and give the relation between concentration  $c$  and distance  $x$  from center of rotation. Each molecular species is brought out as a step on the  $c$ - $x$  curve (Figure 6).

The change in refractive index can be used in various ways. The simplest way is to apply the Toepler *schlieren* method (80). The different molecular species present are then recorded on the plate like the lines of a mass spectrum (Figure 7).

The most accurate procedure for obtaining the real concentration distribution in the sample studied is to take pictures of a finely ruled scale through the sedimenting column of solution by light of a wave length which is not absorbed (18, 19). By measuring the displacement,  $z$ , of the lines, we get the concentration gradient,  $dc/dx$ , as a function of the distance from the center of rotation. Each molecular species is therefore shown as a maximum on the  $z$ - $x$  curve (Figure 8).

In many cases, such as antibodies, enzymes, mixtures of proteins and carbohydrates, it would be of great value if a mechanical division of the sample studied could be accomplished after a certain time of centrifuging and controlled by optical observations. Analytical determination of sedimentation would then be possible. Experiments of this kind can now be performed using the cell with partition membrane shown in Figure 3 (81). Figure 9 demonstrates the completeness of the separation (pneumococcus antibody).

### Ultracentrifuge Measurements

Two kinds of measurements can be made by means of the ultracentrifuge. In the first place, one may centrifuge long enough for a state of equilibrium to be reached between sedimentation and diffusion. Then for each molecular (or particle) species the following formula is valid (53, 58):

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)} \quad (1)$$

where  $M$  = molecular (or particle) weight,  $R$  = gas constant,  $T$  = absolute temperature,  $c$  = concentration of solute,  $V$  = partial specific volume of solute,  $\rho$  = density of solution,  $x$  = distance from center of rotation, and  $\omega$  = angular velocity.

In this way one obtains the molecular weight directly, independent of shape or hydration (22). If several molecular species are present in the solution the molecular weight values calculated for different distances from the center of rotation show a marked drift. Freedom from drift is a criterion of homogeneity with regard to molecular weight.

In the second place one may use a centrifugal field strong enough to cause the molecules or particles to sediment with measurable velocity. This procedure enables us to find how many different kinds of molecules are present in the solution. If the sedimentation velocity is referred to unit field and water of 20° C. as solvent, it is called the sedimentation constant:

$$s = \frac{dx/dt}{\omega^2 x} \eta/\eta_0 \frac{1 - V\rho_0}{1 - V\rho} \text{ sec.} \quad (2)$$



FIGURE 7. SEDIMENTATION PICTURES FOR LIMULUS HEMOCYANIN (ERIKSSON-QUENSEL)

Obtained by Toepler *schlieren* method at pH 6.8, showing the fastest three sedimenting components of  $s = 56.5 \times 10^{-13}$ ,  $34.6 \times 10^{-13}$ , and  $16.1 \times 10^{-13}$ . Centrifugal force 120,000 times gravity. Time between exposures, 5 minutes



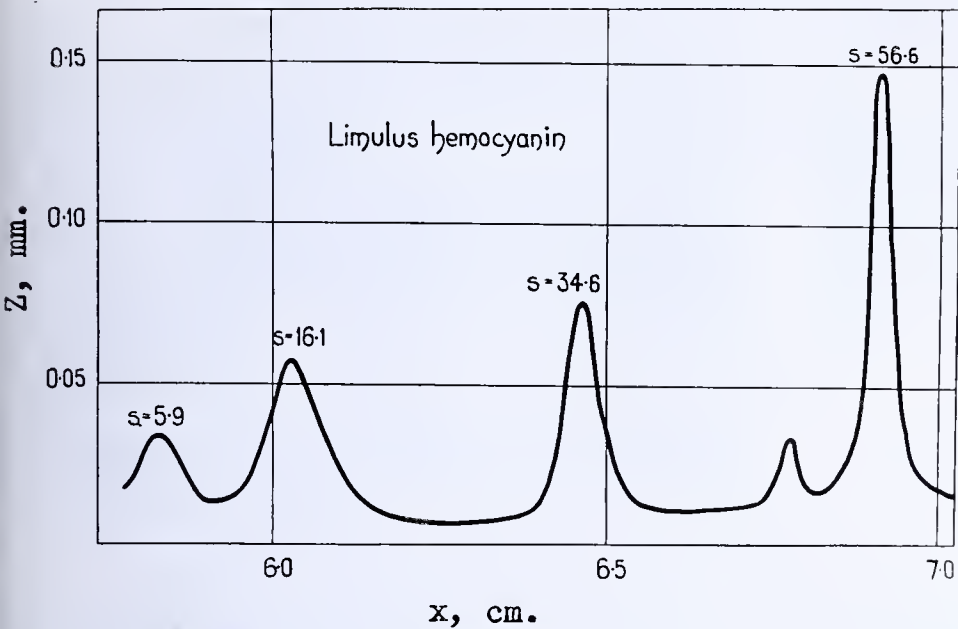


FIGURE 8. SEDIMENTATION DIAGRAM FOR LIMULUS HEMOCYANIN (PEDERSEN)  
Obtained by the refractive index method at pH 6.8, showing the same four main components as in Figure 6 and also a small amount of a fifth. Centrifugal force, 120,000 times gravity. Time after reaching full speed, 35 minutes

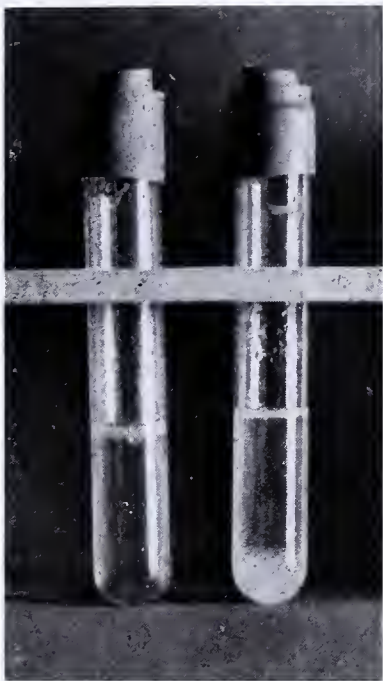


FIGURE 9. ANALYTICAL DETERMINATION OF SEDIMENTATION

Horse antibody serum against pneumococcus Type I polysaccharide. Left. Content of upper cell compartment after addition of polysaccharide. Right. Content of lower cell compartment after addition of polysaccharide

where  $\eta$  and  $\rho$  are the viscosity and density of the solution,  $\eta_0$  and  $\rho_0$  the same quantities for water at 20° C.  
By combining diffusion and sedimentation data the weight of the different molecular species is calculated according to the formula (53, 59)

$$M = \frac{RTs}{D(1 - V\rho)} \quad (3)$$

where  $s$  = sedimentation constant, and  $D$  = diffusion constant.

This equation may be deduced in such a way that the independence of  $M$  of shape and hydration becomes evident.

Both in Equation 3 and in Equation 1 the molar frictional constant is eliminated, in the first case because two independent measurements are carried out, one on sedimentation and one on diffusion, and in the second case because sedimentation and diffusion are responsible for the state of equilibrium reached.

Sedimentation measurements in the ultracentrifuge can also be used for the determination of the weight distribution or size distribution of molecules or particles in a polydisperse mixture (3, 21, 29, 41, 45, 69). As the theory is rather complicated, we will not go into it here.

MEASUREMENT OF DIFFUSION. In order to calculate molecular weight from sedimentation velocity determinations, it is necessary to have an independent and accurate measurement of the diffusion constant,  $D$ . In many cases only a small amount of substance is available and a micromethod has therefore been worked out (18, 20).

The light from a lamp,  $b$ , passes filters,  $c$ , and a transparent scale,  $d$ , on its way to the diffusion vessel,  $f$ , and the camera,  $n$ . A thermostat ensures constant temperature. A diffusion cell with plane-parallel windows and requiring only about 1 cc. of solution is used (Figures 10 and 11).

By means of a movable slide the solvent can be placed on top of the solution. The change of concentration with time at the boundary between the two columns of liquid is then followed optically, by means of either the light absorption or the refraction method.

ELECTROPHORESIS MEASUREMENTS. As a supplement to the study of the sedimentation of molecules in centrifugal

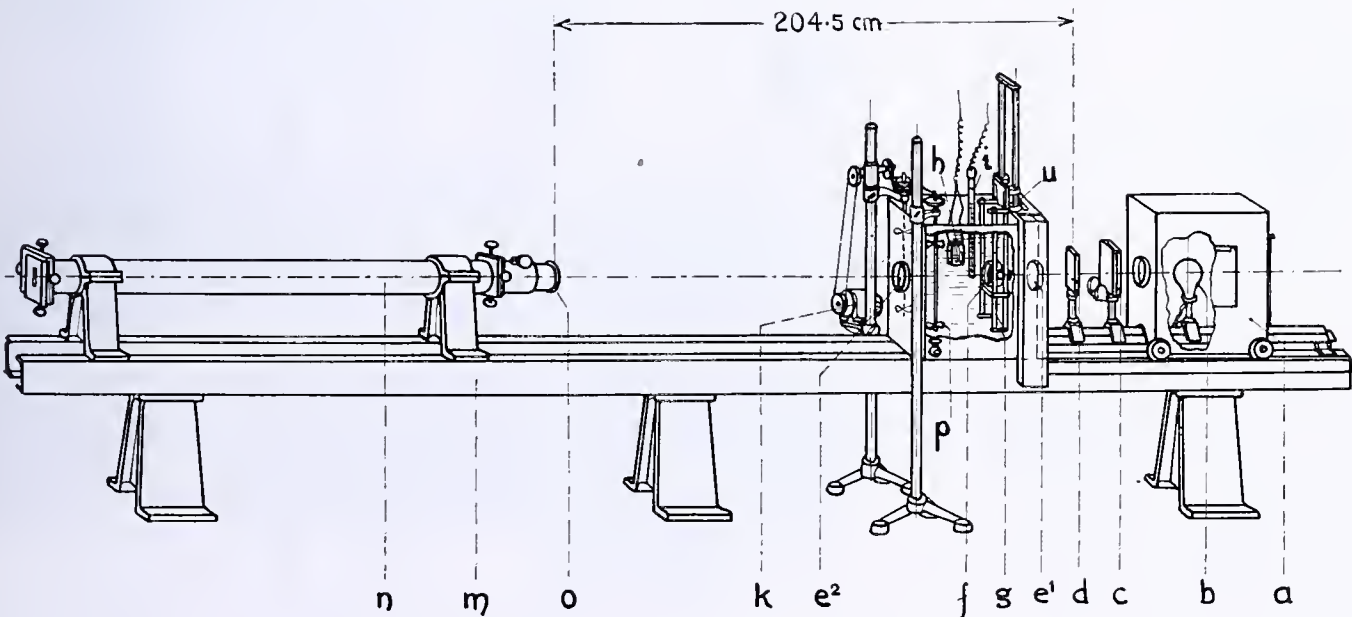


FIGURE 10. DIFFUSION APPARATUS (LAMM)



fields it is of considerable value to be able to investigate their migration in electric fields (71, 76).

The electrophoretic mobility is measured using the moving boundary method. In a U-tube with plane-parallel windows the solution to be studied is placed underneath the solvent and an electric potential gradient is created over reversible electrodes. The movement of the boundary is observed by means of the light absorption or one of the refraction methods. A plot of the mobility as a function of pH furnishes two important data—viz., the isoelectric point and the mobility per pH unit in the isoelectric region.

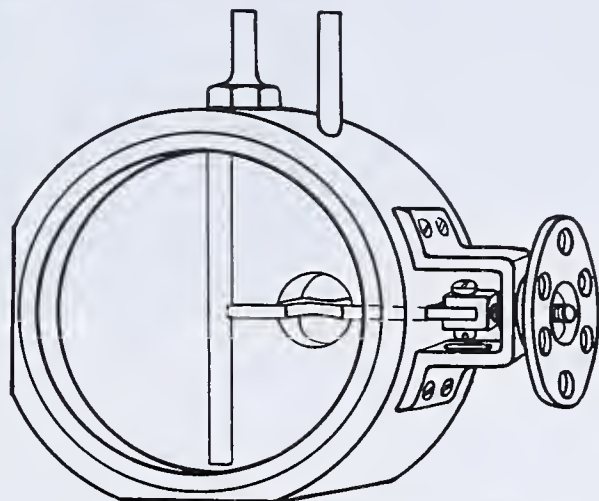


FIGURE 11. DIFFUSION CELL (LAMM)

The general setup for electrophoresis measurements is similar to that used for diffusion determinations. The migration apparatus has recently been very much improved (77).

The straight limbs of the tube are now made rectangular in section, thus offering a larger surface for conducting away the heat. The front walls are plane-parallel, so as to allow accurate optical observations to be carried out. The limbs are divided into two parts which on both ends are cemented to precision ground-glass plates. Corresponding plates are also cemented to adjacent top and bottom parts of the U-tube. This makes it possible to divide the column of solution after a suitable migration time. In order to minimize the danger of thermal convection currents and at the same time allow higher voltages to be applied, the electrophoresis is conducted at about 4° C. where water has its density maximum and where the change of density with temperature, therefore, is zero. A further feature of considerable importance for the analysis of mixtures consists in giving the whole column of liquid in which the electrophoretic migration takes place a constant motion so as to prevent the boundaries from moving out from the straight limbs of the U-tube in long-timed experiments. To this end an ebonite cylinder is slowly lifted out of the liquid in one of the electrode vessels by means of clock-work.

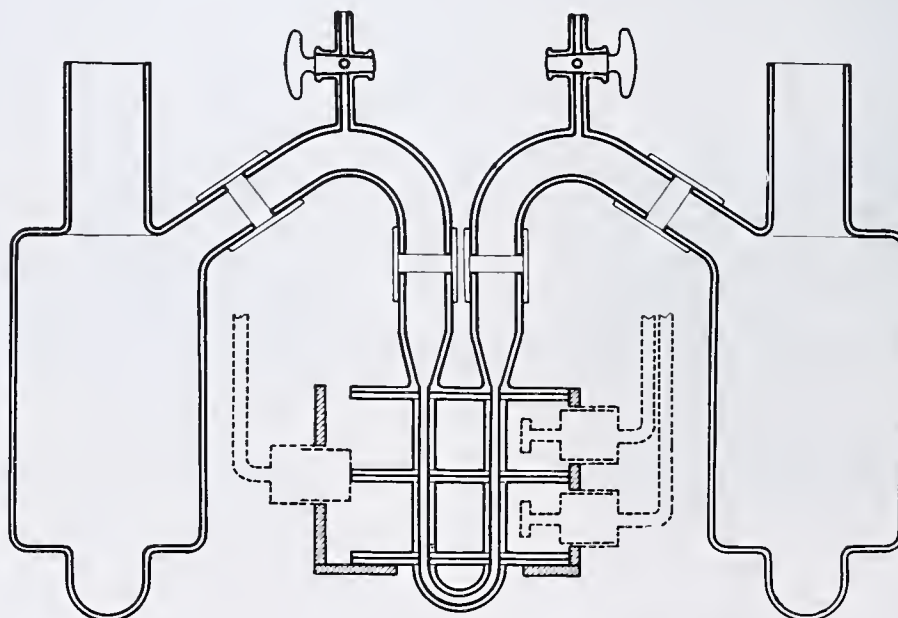


FIGURE 12. ELECTROPHORESIS CELL (TISELIUS)

**APPLICATIONS.** The ultracentrifuge has a wide range of application. With the aid of this tool molecular weight determinations have been done from about 20,000,000 (tobacco mosaic virus) down to about 40 (lithium chloride). This technic offers the unique possibility of carrying out an analysis of the various molecular species or particle sizes present in a solution. The sedimentation constant is a very characteristic molecular property and, by means of it, it is often possible to follow sensitive aggregation and dissociation reactions in biological systems. The combination of sedimentation equilibrium and sedimentation velocity measurements allows certain conclusions with regard to the shape of the molecules or particles. This is often of importance when investigating high-molecular compounds.

Among the substances studied so far are proteins, polysaccharides, polyhydrocarbons, polystyrenes, dyestuffs, and other synthetic organic compounds, as well as inorganic colloids and inorganic salts.

### Results of Protein Investigations

Some of the main results of the protein investigations carried out in Upsala may be mentioned (48, 50, 52, 54).

A very striking but rather unexpected property of protein solutions discovered by the ultracentrifugal analysis is the perfect molecular homogeneity. This means that the solution of a certain protein is either uniform with regard to molecular weight or contains a limited number of different molecular species, as a rule in equilibrium with each other. Change in protein concentration, in pH, or in concentration of other solutes present may bring about dissociation or association.

If the sedimentation proceeds so quickly that no appreciable diffusion takes place during a run, the molecular homogeneity can be tested simply by studying the degree of sharpness of the receding boundary (Figures 13 and 14).

In cases where the sedimentation proceeds more slowly, so that noticeable diffusion occurs during a run, the homogeneity can be tested by comparing the theoretical sedimentation-diffusion curves with the observed ones (Figure 15).

A homogeneity test may also be performed by means of sedimentation equilibrium measurements (Figure 16). Here the molecular weight values should be independent of the distance from center of rotation.

The dependence of a protein on pH is exemplified by the stability diagrams of *Helix pomatia*, *Helix arbustorum*, *Helix nemoralis*, and *Helix hortensis* (Figure 17, 11).

In the case of *Helix pomatia* and *Helix nemoralis* the protein contains only one component at the isoelectric point, while the hemocyanin of *Helix arbustorum* and *Helix hortensis* contains two components in the isoelectric region. On lowering or raising the pH, points are reached where a very small change in pH causes a great change in the molecular state. The original molecule of *Helix pomatia* of weight 6,740,000 ( $s = 98.9 \times 10^{-13}$ ) dissociates stepwise into halves ( $s = 62.0 \times 10^{-13}$ ), eighths ( $s = 16.0 \times 10^{-13}$ ), and sixteenths ( $s = 12.1 \times 10^{-13}$ ). The pH-dissociation products represent perfectly homogeneous com-



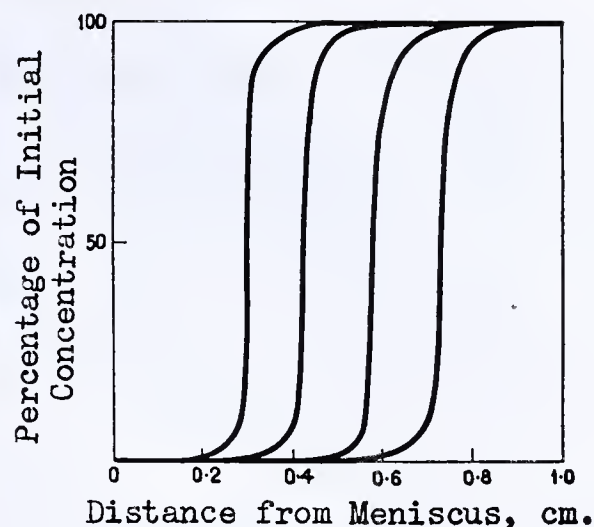


FIGURE 13. SEDIMENTATION PICTURES OBTAINED BY ABSORPTION METHOD (LEFT), AND CURVES OF CONCENTRATION DISTRIBUTION FOR *HELIX* HEMOCYANIN AT pH 5.5 (RIGHT)

$M_n = 6,740,000$ ;  $s = 98.9 \times 10^{-13}$ . Centrifugal force 45,000 times gravity. Time between exposures, 5 minutes. Sharpness of boundary and steepness of curves demonstrate the high degree of molecular homogeneity of this protein (Eriksson-Quensel).

ponents. The presence of divalent ions ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ) causes a considerable change in the stability diagram of *Helix pomatia* hemocyanin. Measurements of the Tyndall effect gave the first indication of this interesting phenomenon (9). An analysis by means of the ultracentrifuge (Eriksson-Quensel) has shown that upon addition of 0.01 *M* calcium chloride, the dissociation on the alkaline side of the isoelectric point does not become noticeable until a pH of about 9.5 is reached, where the molecule splits into halves and eighths. Without  $\text{Ca}^{++}$  the dissociation starts at pH 7.4.



FIGURE 14. SEDIMENTATION OF HEMOGLOBIN IN CENTRIFUGAL FIELD 900,000 TIMES GRAVITY (ERIKSSON-QUENSEL)

Time between exposures, 3 minutes

The reversibility of the dissociation-association process influenced by hydrogen-ion concentration is demonstrated by the following experiment (11):

A solution of *Helix pomatia* hemocyanin at pH 6.8 of sedimentation constant  $98.9 \times 10^{-13}$  (molecular weight 6,740,000) was brought to pH 8.0, where it contains three components with the sedimentation constants  $98.9 \times 10^{-13}$ ,  $62.0 \times 10^{-13}$ , and  $16.0 \times 10^{-13}$  (molecular weights 6,740,000, 3,370,000, and 342,000). The pH was then changed back to 6.8 and a sedi-

mentation analysis performed. It was found that all the fragments of dissociation had completely united to form the original component of  $s = 98.9 \times 10^{-13}$  (molecular weight 6,740,000).

High dilution often causes dissociation. Thus, hemoglobin is partly dissociated into half molecules upon dilution (35). In dilute solutions of thyroglobulin there are present several dissociation products (23). The addition of an amino acid or another protein often causes dissociation (33). Thus serum albumin may be split by adding clupein (Figure 18).

In certain cases even extremely small amounts of foreign substances may cause dissociation. Thus, the addition of 0.001 per cent thyroxine gives rise to an appreciable dissociation of thyroglobulin (24).

The action of a dissociating compound on a protein is more or less specific. An amino acid which acts strongly upon a certain protein may have no effect on another protein, and vice versa. Thus arginin plus ammonium chloride dissociates serum albumin (Figure 19) but not *Helix* hemocyanin, while lysin plus ammonium chloride splits the latter protein but not the former (10, 34). Guanidine chloride affects *Helix* hemocyanin very strongly but has only a very slight effect on serum albumin. Clupein splits both, and arginin without ammonium chloride has no effect on either (10, 33, 34).

High salt concentration may cause dissociation or association. In solutions of thyroglobulin ( $s = 19.2 \times 10^{-13}$ ,  $M = 640,000$ ), the addition of 4 *M* sodium chloride gives rise to a homogeneous association product of  $s = 196 \times 10^{-13}$ , corresponding to a molecular weight of about 16,000,000 (23, 24).

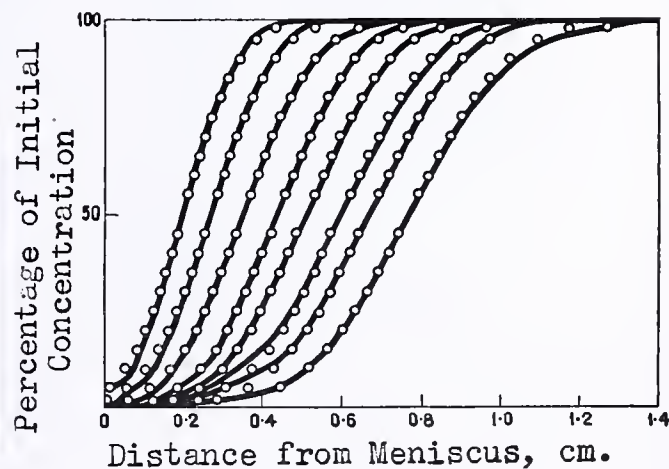


FIGURE 15. SEDIMENTATION PICTURES OBTAINED BY ABSORPTION METHOD (LEFT) AND CURVES OF CONCENTRATION DISTRIBUTION FOR  $\alpha$ -LACTALBUMIN (KEKWICK) (RIGHT)

$M_n = 17,600$ ;  $s = 1.9 \times 10^{-13}$ ;  $D = 10.6 \times 10^{-7}$ . Observed (full-drawn curve) and theoretical (circles) values agree, showing that  $\alpha$ -lactalbumin is homogeneous with regard to molecular weight. Centrifugal force, 310,000 times gravity. Time between exposures, 40 minutes (Pedersen)



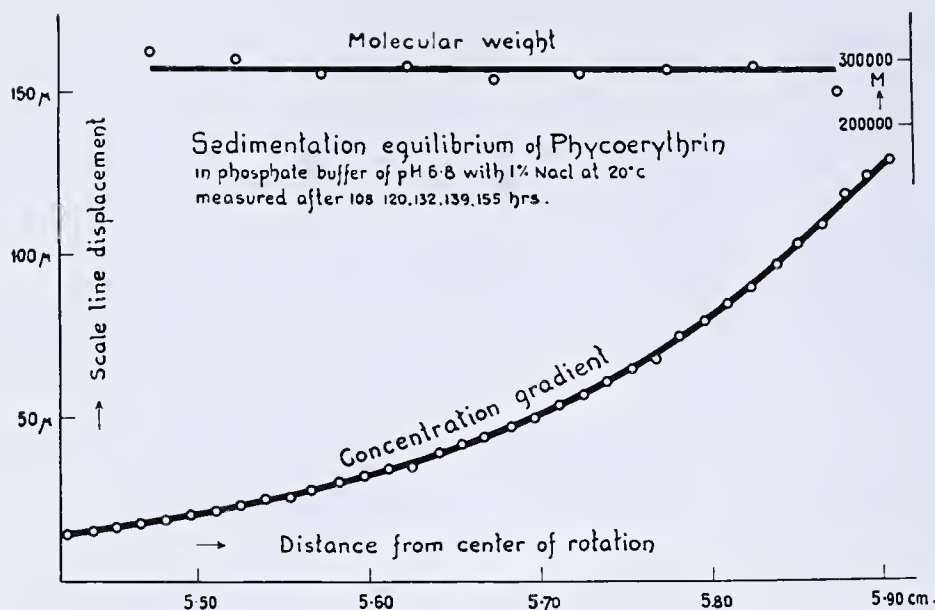


FIGURE 16. RELATION BETWEEN MOLECULAR WEIGHT AND DISTANCE FROM CENTER OF ROTATION FOR PHYCOERYTHRIN ( $M = 290,000$ ) AT PH 6.8 (ERIKSSON-QUENSEL)

Constancy of molecular weight throughout the whole  $x$ -region demonstrates homogeneity of this protein.

Recently it has been found that a protein molecule may be split by the action of ultrasonic waves (8). Thus, Helix hemocyanin at pH 6.2 is partly decomposed into half molecules. This process seems to be different from the pH dissociation, in so far as a lowering of pH does not cause the half molecules to unite.

### Special Groups of Proteins

The above survey has aimed at giving a general picture of the physico-chemical properties of the protein molecules, especially with regard to the influence of environment. In the following, a short summary of some of the results obtained in Upsala for special groups of proteins will be presented.

The serum proteins are among those which have been most fully studied, but which still present notable difficulties. Early sedimentation studies (27) in the ultracentrifuge showed that in dilute normal serum there are two main protein constituents with  $s = 4.5$  and  $7.1$  corresponding to the albumin ( $s = 4.5$ ,  $D = 6.2$ ,  $M = 69,000$ ) and globulin ( $s = 7.1$ ,  $D = 4.05$ ,  $M =$  about  $160,000$ ) fractions of the salting-out process and a small amount of a heavier globulin component of  $s = 18.5$ . In pathological sera new components often appear side by side with the normal ones (27).

A detailed study (McFarlane, Pedersen, and Tiselius) brought to light a number of new facts. It was found (25) that in concentrated sera, part of the globulin molecules dissociated and that this effect was probably due to the action of serum albumin (33, 34). The effect is different for different species. In Figure 20 sedimentation diagrams for normal human, cow, and horse serum are given.

In diluted condition all three show the maxima of normal albumin and globulin, the globulin content decreasing in the order: horse, cow, man. In the undiluted sera the globulin maximum is very much depressed and there appears in one of the diagrams (human serum) a new maximum (the "X-component," 25) probably corresponding to half or fourth molecules of globulin (34). In the horse and cow sera this dissociation product is hidden in the albumin maximum.

A comparison of normal human serum with pathological sera reveals a number of interesting differences (Figure 21, 26).

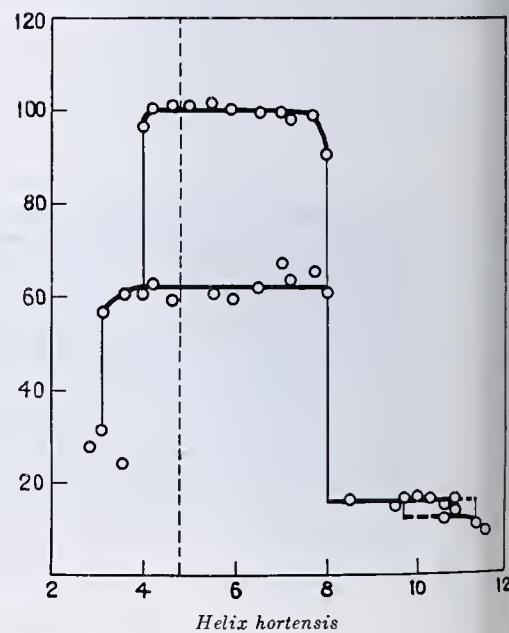
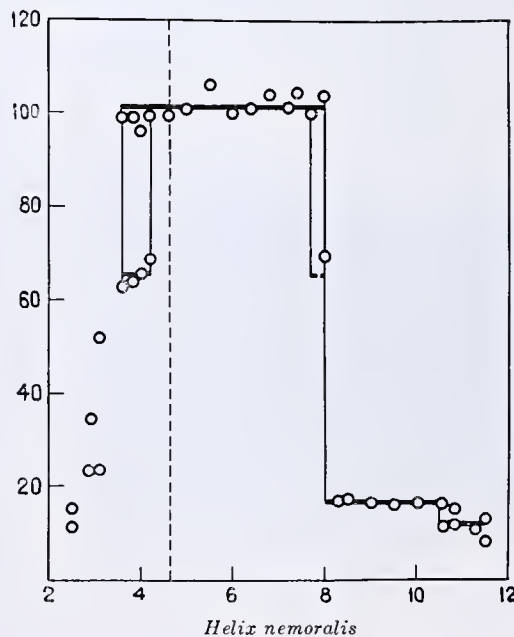
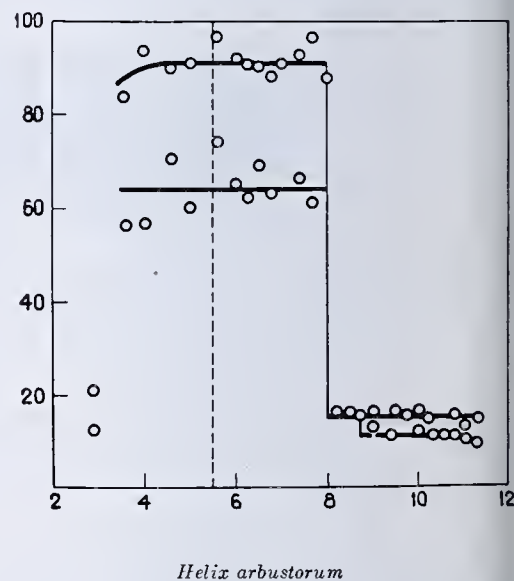
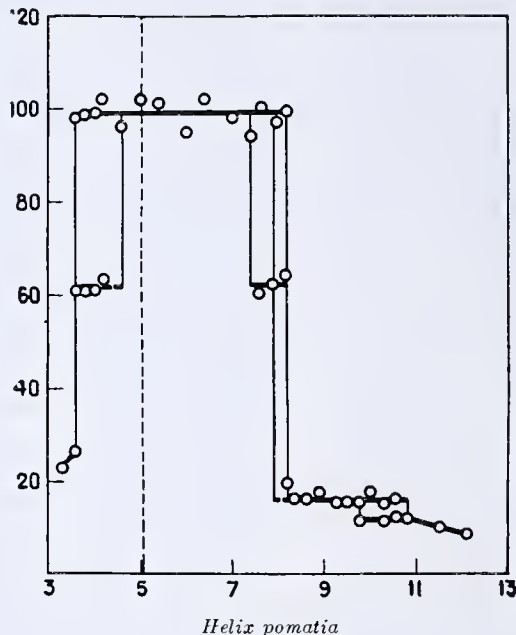


FIGURE 17. pH-STABILITY DIAGRAMS (ERIKSSON-QUENSEL)



In the first place the globulin content is usually very much increased, as is also the  $\alpha$ -component. Sometimes new components appear (Figure 21, malignant tumor of bile duct). In the case of certain diseases of the kidney (Figure 21, nephritis) the albumin maximum is unsymmetrical, indicating the presence of molecules of lower molecular weight than serum albumin (possibly dissociation products). The globulin

content often increases during a disease, probably as a result of increasing immunization (Figure 21, scarlatina). The possibility of using ultracentrifugal analysis for diagnostic purposes is being tested by McFarlane at the Lister Institute, London.

Ultracentrifugal studies of immune sera and purified antibodies (13) have shown that the antibody activity is carried by a globulin component of one of the sedimentation constants found in normal sera. Thus the antibody to Type III pneumococcus polysaccharide obtained from rabbit serum and containing 90 per cent specifically precipitable protein gave the normal serum globulin sedimentation constant

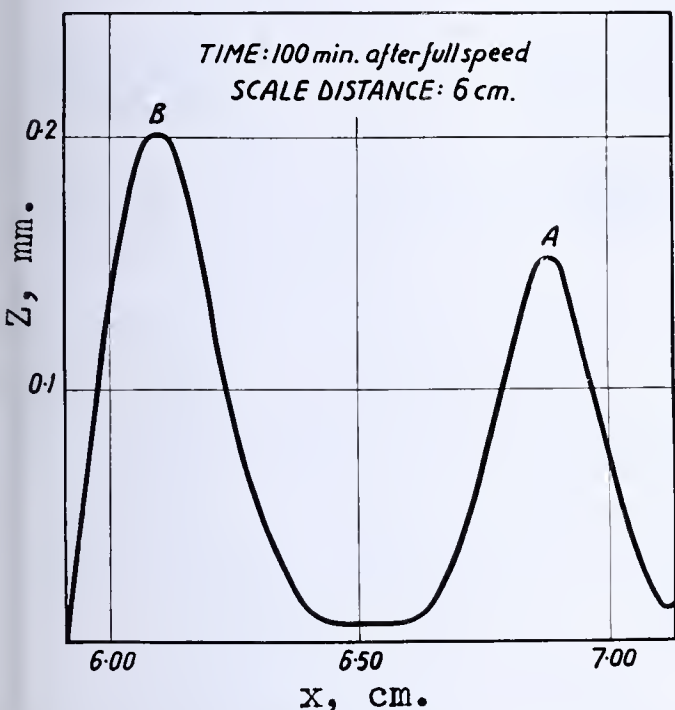


FIGURE 18. SEDIMENTATION DIAGRAM OF SERUM ALBUMIN IN 2.6 PER CENT CLUPEIN SOLUTION (PEDERSEN)

Rapidly sedimenting main maximum, A, represents undissociated protein; slowly sedimenting maximum, B, is dissociation product  $s \sim 1 \times 10^{-13}$  and  $M \sim 1/8$  that of serum albumin. Sedimentation of clupein itself has been subtracted from curves.

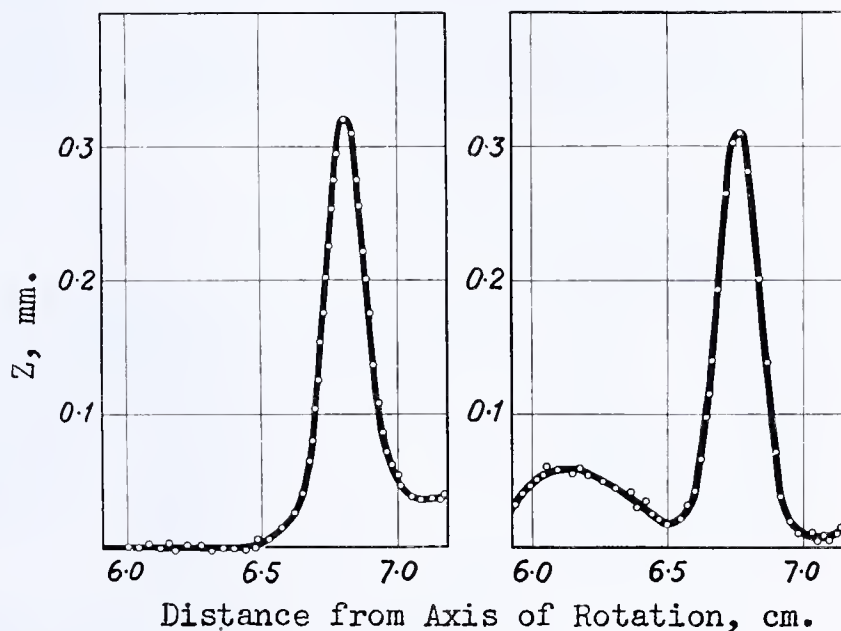


FIGURE 19. SEDIMENTATION DIAGRAM OF SERUM ALBUMIN IN 2.6 PER CENT ARGININ SOLUTION AT pH 5 (PEDERSEN)

Left. Without ammonium chloride  
Right. After addition of ammonium chloride to 0.1 M.

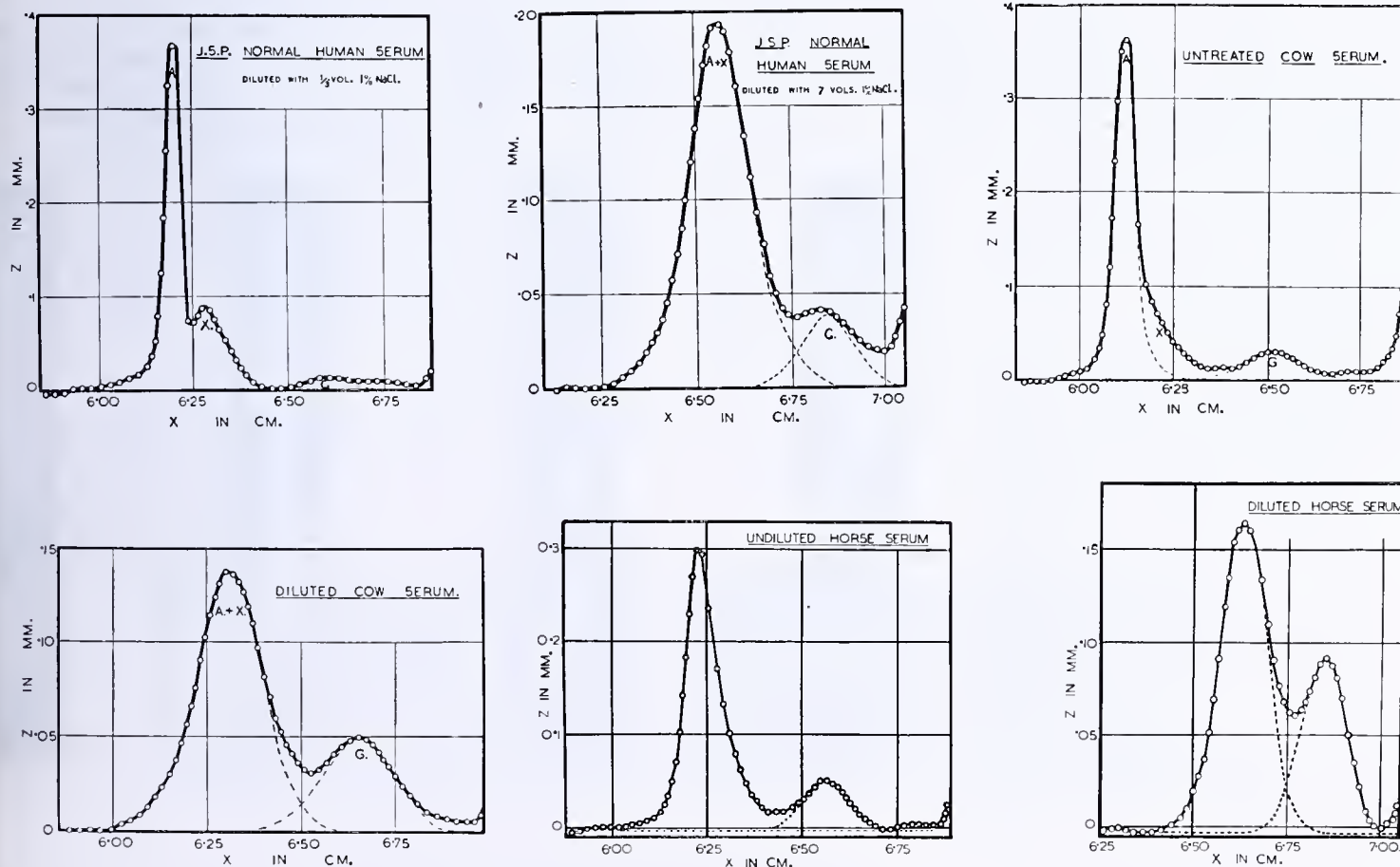


FIGURE 20. SEDIMENTATION DIAGRAMS OF UNDILUTED AND DILUTED NORMAL SERUM FROM MAN, COW, AND HORSE (McFARLANE)



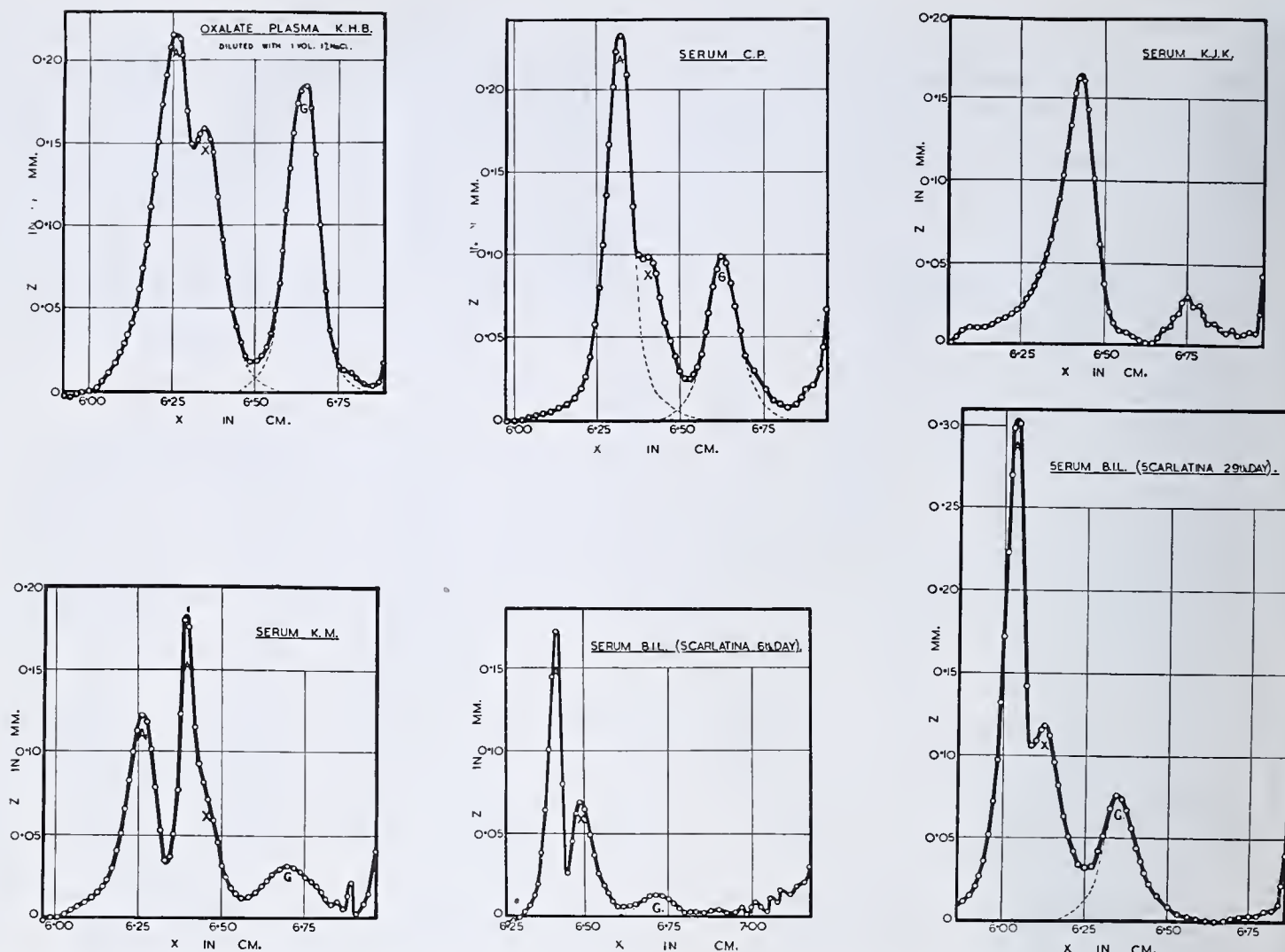


FIGURE 21. SEDIMENTATION DIAGRAMS OF PATHOLOGICAL HUMAN SERA (McFARLANE)

K. H. B. Pulmonary tuberculosis C. P. Ulcerative condition in rectum K. J. K. Nephritis K. M. Tumor of bile duct B. I. L. Scarlatina

( $s = 7$ ); so did an anti-egg-albumin globulin (precipitable to 50 per cent). A highly purified antibody to Type I pneumococcus carbohydrate isolated from horse serum showed almost homogeneous sedimentation with the constant 18. A component of this sedimentation is present to a small amount in normal sera, as already pointed out. There would thus appear to be a fundamental difference in the mechanism of the formation of pneumococcus anticarbohydrate in the horse and in the rabbit.

The application of an improved electrophoresis technic to the study of the serum proteins has given very interesting results (75). Thus in normal serum four electrochemically well-defined proteins were found—viz., one albumin and three globulins,  $\alpha$ ,  $\beta$ ,  $\gamma$  (Figure 22).

The globulins have approximately the same molecular weight but different electrochemical properties—e. g., the isoelectric point of globulin  $\gamma$  is at pH 6.0 instead of 5.1 as for the  $\alpha$  and  $\beta$  components. In addition, the mobilities are different, especially in the alkaline region. A separation by means of electrophoresis is therefore comparatively easy. Investigation of a highly potent anti-egg-albumin serum from a rabbit showed that the antibody function migrated with the  $\gamma$ -globulin frac-

tion only. By isolation of this fraction a considerable concentration (85 per cent) of specifically precipitable protein could be obtained. In a Type I antipneumococcus horse serum Tiselius and Kabat (79) found a new globulin com-

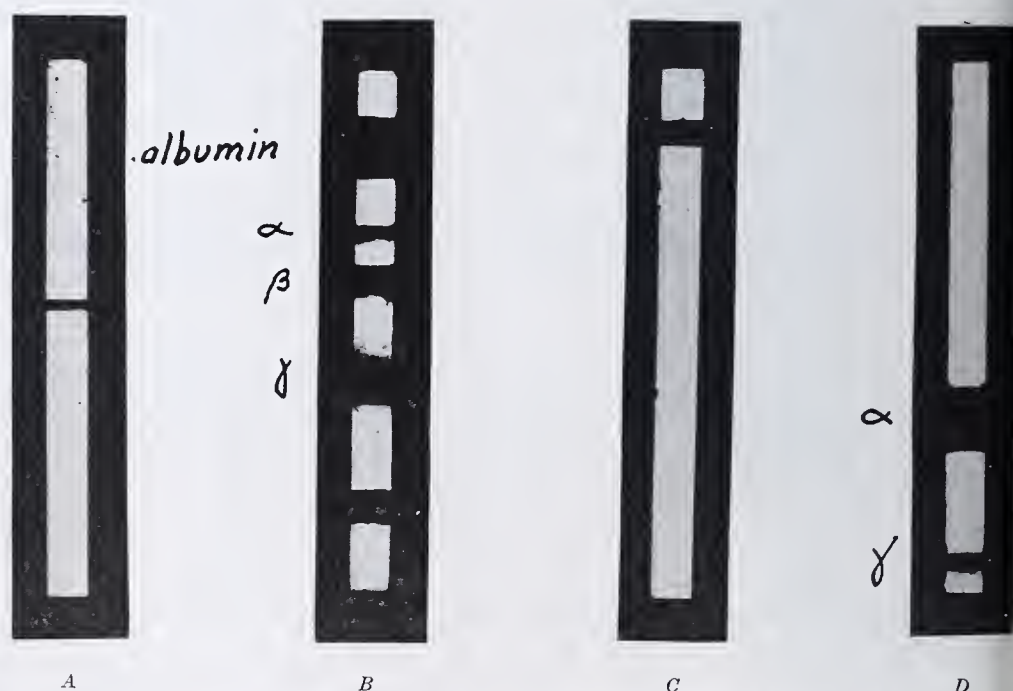


FIGURE 22. PHOTOGRAPHS OF MIGRATING BOUNDARIES (TISELIUS)

- A. Homogeneous protein (crystallized ovalbumin)  
 B. Horse serum after 80 minutes at 7.25 volts per cm.  
 C. Serum albumin, isolated from serum by electrophoresis. Same time and voltage as in B  
 D. Pseudoglobulin, isolated from serum by salting out and subsequent electro-dialysis



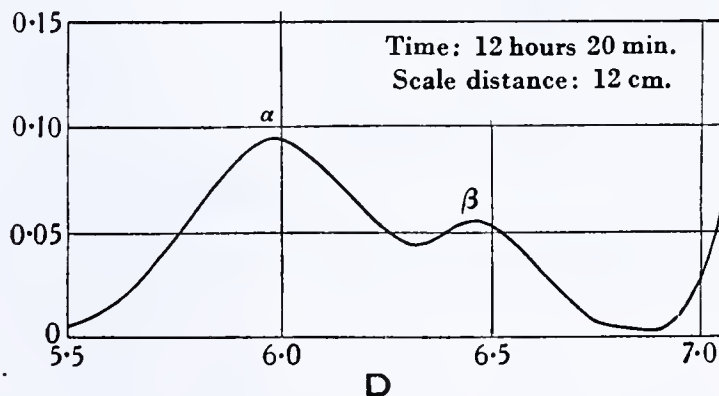
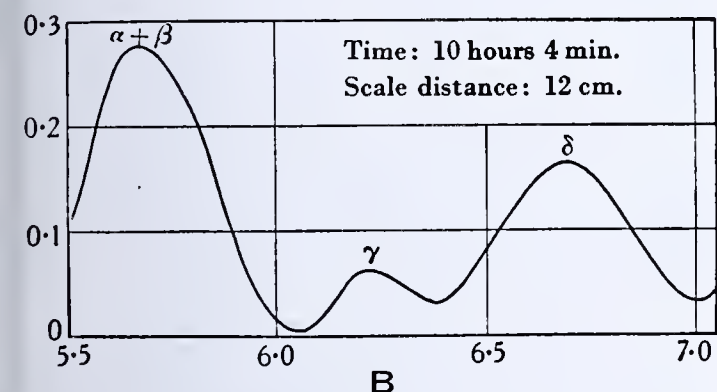
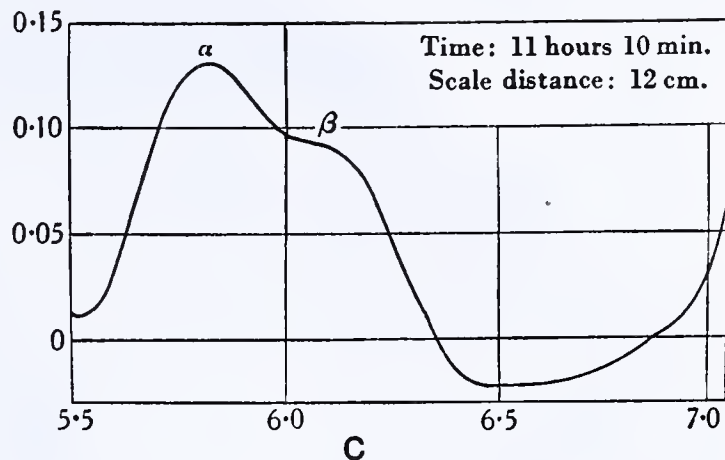
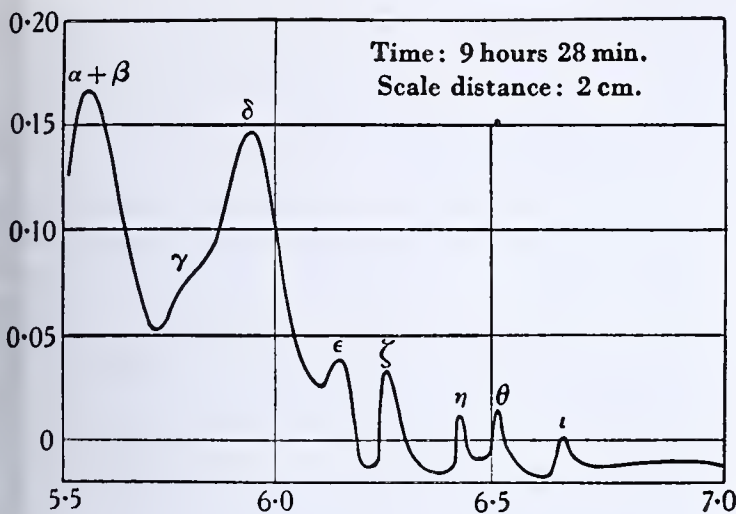


FIGURE 23. SEDIMENTATION CURVES FOR PROTEINS IN COW'S MILK (PEDERSEN)

Obtained by refractive index method. *A* represents 13 minutes, *B* 49 minutes, *C* 115 minutes, and *D* 185 minutes after reaching full speed. In *A*, no separation of the molecular species  $\alpha$ - and  $\beta$ -lactalbumins can be noticed.  $\gamma$ -Lactoglobulin is just visible as a hump on the curve.  $\delta$ -Casein has developed an incomplete maximum, and  $\epsilon$ ,  $\zeta$ ,  $\eta$ ,  $\theta$ , and  $\iota$ -casein are represented by separate maxima. In *B*, the maximum  $\alpha + \beta$  begins to develop a dissymmetry,  $\gamma$  is clearly visible,  $\delta$  is well separated, and  $\epsilon$ ,  $\zeta$ ,  $\eta$ ,  $\theta$ , and  $\iota$  have sedimented down completely. In *C*,  $\beta$  is seen as a hump on the curve,  $\delta$  and  $\gamma$  have sedimented down completely. In *D*,  $\alpha$  and  $\beta$  are well separated.

ment, migrating between the  $\beta$ - and the  $\gamma$ -globulin. This component completely disappeared from the electrophoresis diagram after specific precipitation with Type I polysaccharide, whereas the others were not changed, proving that the antibody function is carried only by this new globulin. Therefore horse and rabbit antisera, also from the electrophoresis point of view, seem to be radically different.

The milk proteins are very complex and have not yet been fully disentangled. In cow's milk of normal pH the casein is present as a polydisperse, rather coarse suspension of Caseinogenate, which sediments rapidly in the ultracentrifuge. The milk serum thus formed there are (according to recent investigations by Pedersen, 30) three proteins:  $\alpha$ -lactalbumin of sedimentation constant 1.9 and diffusion constant 6 and molecular weight 17,500 (first isolated by Kekwick);  $\beta$ -lactalbumin (also called Palmer's lactoglobulin) of  $s = 2$ ,  $D = 7.27$ , and  $M = 39,000$ . Then there is a typical

globulin of  $s = 7.2$  and a molecular weight probably around 140,000.

If skim milk is dialyzed against phosphate buffer of pH 6.8 the casein dissolves and a solution of all the milk proteins is obtained. The casein is polydisperse and of a very complex nature; its dispersity is dependent upon its concentration. Figure 23 gives some sedimentation diagrams for cow's milk obtained by means of the refractive index method showing the two albumins  $\alpha$  and  $\beta$ , the globulin  $\gamma$ , and the caseins,  $\epsilon$ ,  $\zeta$ ,  $\eta$ ,  $\theta$ , and  $\iota$ .

The respiratory proteins are of great interest not only because of their unique physiological importance but also from a physico-chemical point of view. Respiration being of a two-fold nature—cellular or inner respiration and external respiration located in the blood—we distinguish between respiratory cell proteins and respiratory blood proteins.

Three proteins active in cellular or inner respiration have



FIGURE 24. SEDIMENTATION OF POLYDISPERSE POLYSTYRENE (SIGNER)

A. Interaction of the molecules  
B. Free sedimentation



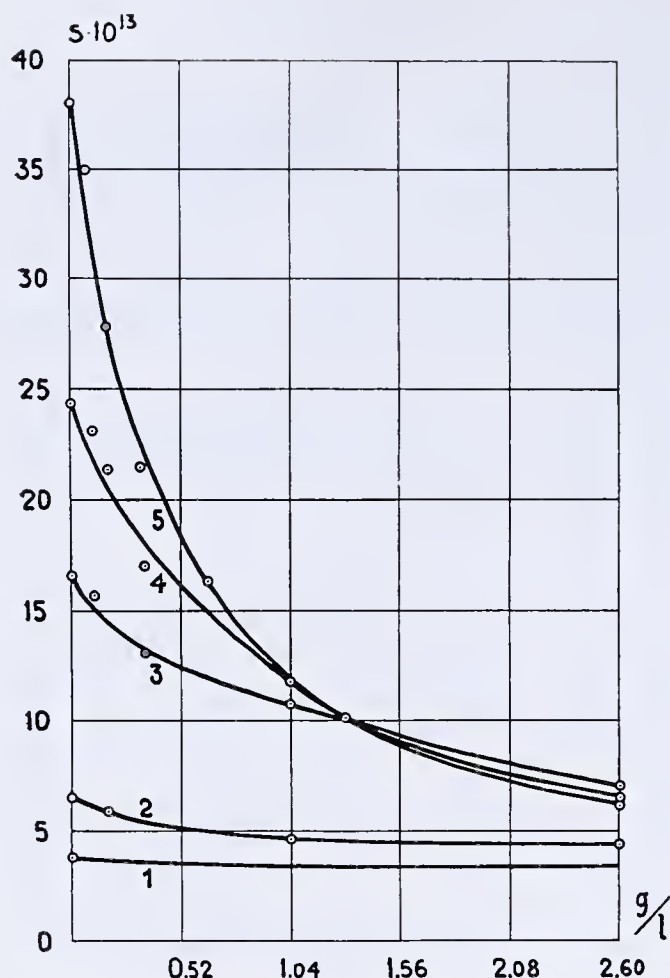


FIGURE 25. CONCENTRATION EFFECT ON SEDIMENTATION CONSTANTS OF POLYSTYRENE FRACTIONS (1, 2, 3, 4, 5) OF INCREASING MOLECULAR WEIGHT (SIGNER)

been studied—viz., Keilin's cytochrom C, Warburg's yellow enzyme, and myoglobin (often called muscle hemoglobin). Of these perhaps only the first two are true respiratory cell proteins taking part in the enzymatic oxidation-reduction reactions. Myoglobin is more like the blood pigments, taking up and giving off oxygen along a dissociation curve. It probably serves as an oxygen reservoir for the organism.

Cytochrom C and myoglobin, both of which contain iron in their prosthetic group, have almost the same molecular weight of about 17,000 (35, 38, 73). Their molecular weight is equal to the weight of the *Lampetra* erythrocrucorin and is one-fourth the weight of normal hemoglobin of vertebrates. The yellow enzyme contains one prosthetic group (lactoflavin-monophosphoric acid) per molecule of weight 80,000 (15).

The proteins active in external respiration—the respiratory blood proteins—are numerous and a large number of them have been studied (11, 65). They fall into four classes—red pigments (erythrocrucorins, hemoglobins), green pigments (chlorocrucorins), blue pigments (hemocyanins), and pigments of reddish brown color (hemerythrins). The first two classes have similar prosthetic groups containing iron and are called hematic chromoproteins. For each atom of iron one molecule of oxygen is taken up. The third class has a prosthetic group containing copper and these proteins take up oxygen in the proportion one molecule of oxygen to two atoms of copper. The prosthetic group of the fourth class, the hemerythrins, contains iron as is the case with

the proteins of the first two classes, but the oxygen-binding capacity is one oxygen molecule to three atoms of iron.

One of the most striking points is the fact that low sedimentation constant and, therefore, comparatively small molecular weights are (with one exception) found only for pigments enclosed in blood corpuscles, while the respiratory proteins which occur dissolved in the plasma are characterized by high sedimentation constant and consequently by large molecular weights. The corpuscles of all the vertebrates with the exception of the species belonging to the lower class, the Cyclostomata, contain a pigment of the same molecular weight 68,000 (hemoglobin) with four atoms of iron per molecule. The protein from the Cyclostomata corpuscles has a molecular weight one-quarter of that of hemoglobin, and certain invertebrates have corpuscle erythrocrucorin of one-half the hemoglobin weight (A. Hedenius). The mammalian hemoglobin dissociates reversibly into half molecules upon addition of certain amino compounds such as urea, acetamide, and formamide (47). As shown by Anson and Mirsky (1), it is possible to resynthesize hemoglobin from globin and heme, and this synthetic pigment has proved identical with the native protein with regard to molecular mass. The isoelectric point is slightly lower and the chemical processes used seem, therefore, not to have left it entirely unchanged (12). Erythrocrucorins of high molecular weight occur in the blood plasma of the crustacean *Daphnia* ( $M = 400,000$ ), the snail *Planorbis* ( $M = 1,600,000$ ), and certain worms, *Arenicola*, *Lumbricus* ( $M = 3,200,000$ ).

The hemocyanins form an interesting class with a number of inner connections. The molecular weights of the hemocyanin molecules found in the blood of a certain species are always simple multiples of the lowest well-defined component. Thus, for the Malacostraca the relationship is 1:2 and for the Gastropoda 2:8:16:24. Moreover, the weights of all the well-defined hemocyanin molecules seem to be simple multiples of the lowest among them. In most cases the hemocyanin components of a certain species are interconnected by reversible, pH-influenced dissociation-association reactions. At certain pH values a profound change in the number and percentage of the components takes place. The shift in pH necessary to bring about reaction is not more than a few tenths of a unit. Consequently, the forces holding dissociable parts of the molecule together must be very feeble.

Not only the molecular weights of the hemocyanins but also the mass of most protein molecules—even those belonging to chemically different substances—show a similar relationship. This remarkable regularity points to a common plan for building up the protein molecules. Certain amino

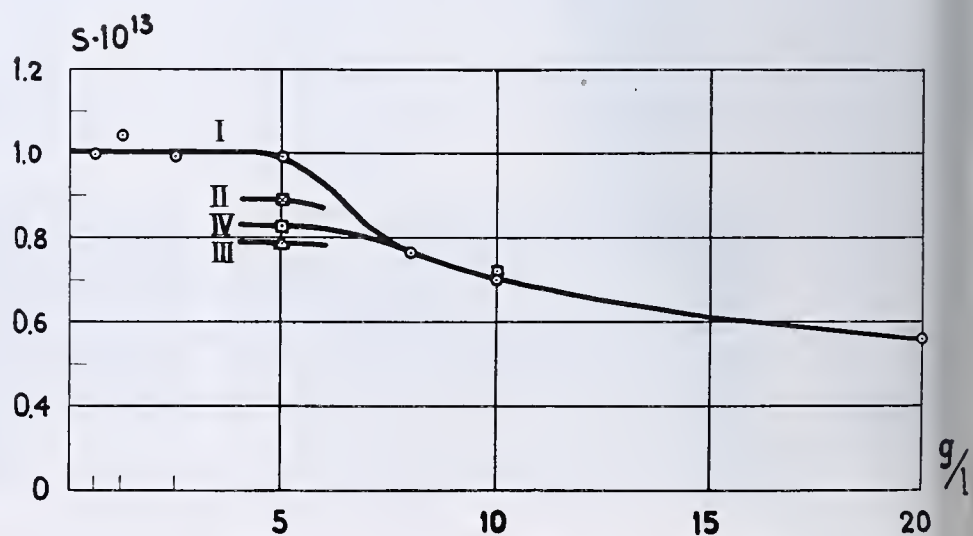


FIGURE 26. METHYL CELLULOSE FRACTIONS (SIGNER)  
Effect of concentration on sedimentation constant



TABLE I. MOLECULAR CONSTANTS OF PROTEINS

$S_{20}$	= sedimentation constant in units of $10^{-13}$ reduced to water at $20^{\circ}$ C.								
$D_{20}$	= diffusion constant in units of $10^{-7}$ reduced to water at $20^{\circ}$ C.								
$M_s$	= molecular weight computed from sedimentation velocity and diffusion measurements								
$M_e$	= molecular weight computed from sedimentation equilibrium measurements								
$M_{calc.}$	= molecular weight calculated from the rule of simple multiples								
$f/f_0$	= ratio of experimentally determined molar frictional constant to molar frictional constant calculated for a spherical particle of the same mass								
$\frac{du}{dpH_0}$	= slope of mobility curve in the vicinity of the isoelectric point								
Protein	$S_{20}$	$D_{20}$	$M_s$	$M_e$	$M_{calc.}$	$f/f_0$	Isoelectric Point	$\frac{du}{dpH_0} \times 10^5$	
Erythrocrucorin (Lampetra)	1.87	10.65	17,100	19,100	17,600 = $\frac{1}{2} \times 35,200$	1.2	5.60	3.2	(34, 38, 63)
Lactalbumin $\alpha$	1.9	10.6	17,500	....		1.2	5.12	6.7	(30, 38)
Cytochrome C	1.89	10.13	15,600	....		1.3	9.7	..	(35, 74)
Myoglobin	2.04	11.25	17,200	17,500		1.1	7.0	7.0	(38, 72)
Glialin	2.00	6.72	26,000	....		1.6	..	..	(2, 38)
Hordein	2.0	6.5	27,000	....		..	..	..	(39)
Zein	1.9	4.0	35,000	....	35,200	..	..	..	(82)
Erythrocrucorin (Arca)	3.46	...	...	33,600		1.0	..	..	(63)
Erythrocrucorin (Chironomus)	2.00	...	...	31,400		1.6	5.40	3.6	(34, 63)
Lactoglobulin	3.12	7.27	41,800	37,900		1.2	5.19	11.9	(30, 38)
Pepsin	3.3	9.00	35,500	39,200		1.1	..	..	(10, 36, 38)
Insulin	3.47	8.20	40,900	35,100		1.1	..	..	(46)
Bence-Jones $\alpha$	3.55	...	...	35,000		1.0	5.20	5.8	(70, 76)
Bence-Jones $\beta$	2.85	7.33	37,700	...		1.3	5.46	3.5	(35, 38)
Egg albumin	3.55	7.76	43,800	40,500		1.1	4.55	10.4	(20, 34)
CO-hemoglobin (horse)	4.5	6.3	69,000	68,000	70,400 = $2 \times 35,200$	1.2	6.92	7.2	(64, 78)
CO-hemoglobin (man)	4.5	6.9	63,000	...		1.2	7.09	6.4	(20, 34)
Serum albumin (horse)	4.5	6.17	70,200	66,900		1.2	4.80	9.1	(27, 34, 38)
Yellow ferment	5.76	6.28	82,800	77,800		1.2	5.22	6.4	(15, 38)
Serum globulin (horse)	7.1	4.05	167,000	150,000	140,800 = $4 \times 35,200$	1.4	$\alpha, \beta = 5.1,$ $\gamma = 6.0$	..	(10, 27, 75)
Phycocyan (Ceranium, dissociation component)	6.2	4.58	131,000	146,000		1.4	4.85	10.2	(10, 34, 38)
Phycocerythrin (Ceranium)	12.0	4.00	290,000	292,000	282,000 = $8 \times 35,200$	1.2	4.25	14.2	(10, 76, 78)
Phycocyan (Ceranium, main component)	11.4	4.05	272,000	273,000		1.2	4.85	10.2	(10, 34, 78)
Edestin	12.8	3.93	309,000	...		1.2	..	..	(38)
Excelsin	13.3	4.26	294,000	...		1.1	..	..	(38)
Amandin	12.5	3.62	329,000	...		1.3	..	..	(38)
Erythrocrucorin (Daphnia)	16.3	...	...	...	422,000 = $12 \times 35,200$	..	..	..	(63)
Hemocyanin (Pandalus)	17.4	...	...	397,000		1.1	..	..	(11)
Hemocyanin (Palinurus)	16.4	3.4	446,000	447,000		1.2	..	..	(11, 38)
Hemocyanin ( <i>Helix pomatia</i> , dissociation component)	12.1	2.23	503,000	....		1.5	5.05	8.1	(11, 38, 76)
Hemocyanin (Busycon, dissociation component)	13.5	3.29	379,600	....		1.4	4.49	10.7	(11, 34, 38)
Hemocyanin (Eledone, dissociation component)	10.6	2.25	440,000	....		1.9	4.6	14	(11, 34, 38)
Thyroglobulin	19.2	2.65	628,000	650,000		1.5	4.58	11	(14, 38)
Hemocyanin (Nephrops)	24.5	2.79	820,000	...	845,000 = $24 \times 35,200$	1.2	4.64	13.3	(11, 34, 38)
Hemocyanin (Homarus)	22.6	2.78	752,000	803,000		1.3	4.95	18	(11, 34, 38)
Hemocyanin ( <i>Helix pomatia</i> , dissociation component)	16.0	1.82	814,000	797,000		1.9	5.05	8.1	(11, 31, 38)
Hemocyanin ( <i>Helix nemoralis</i> , dissociation component)	16.6	1.92	799,000	....		1.8	4.63	11.4	(11, 31, 38)
Erythrocrucorin (Planorbis)	33.7	1.96	1,636,000	1,539,000	1,690,000 = $48 \times 35,200$	1.4	4.77	10.6	(20, 31, 63)
Hemocyanin (Calocaris)	34.0	...	...	1,329,000		1.2	..	..	(11, 65)
Hemocyanin (Octopus)	49.3	1.65	2,785,000	...	2,960,000 = $84 \times 35,200$	1.4	..	..	(11, 37)
Hemocyanin (Eledone)	49.1	1.64	2,796,000	...		1.4	4.6	14	(11, 34, 38)
Erythrocrucorin (Arenicola)	57.4	...	...	3,000,000	3,380,000 = $96 \times 35,200$	1.3	4.56	16	(31, 62)
Chlorocrucorin (Spirographis)	55.2	...	...	...		..	..	..	(10)
Hemocyanin (Rossia)	56.2	1.58	3,316,000	...		1.4	..	..	(11, 38)
Erythrocrucorin (Lumbricus)	60.9	1.81	3,140,000	2,946,000		1.2	5.28	12.6	(34, 38, 62)
Hemocyanin ( <i>Helix pomatia</i> , main component)	98.9	1.38	6,630,000	2,680,000	6,760,000 = $192 \times 35,200$	1.2	5.05	8.1	(11, 38, 76)
Hemocyanin (Busycon, main component)	101.7	...	...	....		1.2	4.49	10.7	(11, 34)
Hemocyanin (Busycon, aggregation component)	130.4	...	...	....	10,140,000 = $288 \times 35,200$	1.2	4.40	10.7	(11, 34)

acids may be exchanged for others, and this may cause slight deviations from the rule of simple multiples, but on the whole, only a very limited number of masses seems to be possible. Probably the protein molecule is built up by successive aggregation of definite units, but only a few aggregates are stable. The higher the molecular weight the fewer are the possibilities of stable aggregation. The steps between the existing molecules, therefore, become larger and larger as the weight increases. These statements are borne out by Table I, in which are collected recent data for the various constants of protein molecules as determined in Upsala.

### Other Classes of High-Molecular Substances

Among the other classes of high-molecular substances studied by means of the ultracentrifugal technic, those forming linear macromolecules are of special interest. Here belong carbohydrates, hydrocarbons, and many synthetic compounds.

A detailed investigation of the solutions of polystyrenes in various organic solvents has been carried out in Upsala by

TABLE II. MOLECULAR CONSTANTS FOR METHYL CELLULOSE DISSOLVED IN WATER

Fraction	$M_w$	$M_z$	$\beta$	$f/f_0$	$L/d$	$L$	$d$	$s_{calc.}$	$s_{obs.}$	$L_{max.}$
II	38,100	63,800	1.0	4.5	139	1190	8.6	0.86	0.89	1040
III	24,300	35,000	0.8	3.9	109	870	7.9	0.75	0.79	670
IV	14,100	18,300	0.7	3.0	77	560	7.3	0.71	0.83	410

$M_w$  = weight-average molecular weight  
 $M_z$  = line-displacement average molecular weight  
 $\beta$  = nonuniformity coefficient  
 $f/f_0$  = ratio of experimentally determined molar frictional constant to molar frictional constant calculated for a spherical particle of the same mass  
 $L$  = major axis of molecule in Ångström units  
 $d$  = minor axis of molecule in Ångström units  
 $s_{calc.}$  = sedimentation constants in units of  $10^{-13}$  calculated from dimensions and mass of the molecule and the viscosity of solvent  
 $s_{obs.}$  = experimentally determined sedimentation constant in units of  $10^{-13}$   
 $L_{max.}$  = maximum length of molecule calculated from degree of association in Ångström units

Signer (42, 44). The molecules were found to be very elongated, and free movement was observed only in very dilute solutions. This effect increases with increasing molecular weight (Figure 25).



Certain hydrocarbons, such as rubber and polychloroprene, as well as cellulose and cellulose derivatives, have been studied at the du Pont Experimental Station, Wilmington, by Kraemer, Nichols, and their co-workers (16). These substances all form very long molecules. Methyl cellulose was investigated in Upsala by Signer (43). Sedimentation equilibrium and sedimentation velocity measurements gave the results in Table II.

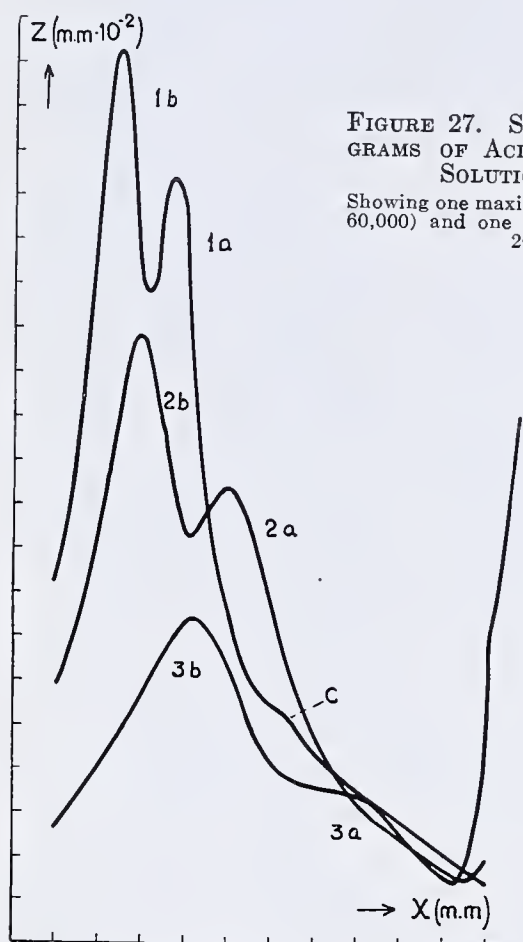


FIGURE 27. SEDIMENTATION DIAGRAMS OF ACID-TREATED STARCH SOLUTIONS (LAMM)

Showing one maximum for amylose ( $M = 60,000$ ) and one for amylopectin ( $M = 200,000$ )

According to Lamm, solutions of starch behave differently in the ultracentrifuge, dependent on their history (17, 18). Polydispersity is the rule. Zinc chloride of 40 per cent strength has the property of dissolving starch in the cold to a comparatively well-defined system of a particle weight around 4,000,000. Heat-treated aqueous solutions have a molecular weight around 100,000, while acid-treated solutions show two maxima (Figure 27) corresponding to an average molecular weight of 60,000 (amylose) and 200,000 (amylopectin).

The dispersity of the amylopectin depends on the kind of treatment with acid to which it has been subjected. By means of electrodialysis the highly polydisperse amylopectin may be removed, leaving the maximum of the more homogeneous amylose.

Glycogen is also polydisperse in aqueous solution. Both the glycogen itself (28) and its methylated derivatives (40) are highly polymerized.

### Inorganic Colloids

Inorganic colloids constituted our first objects of ultracentrifugal study. Extensive investigations on gold sols were carried out by Rinde (41). Even the best colloids prepared by means of the Zsigmondy nuclear method were found to be polydisperse. As an example, Figure 28 gives the size distribution of a very fine-grained sol reduced by phosphorus which served as nuclear solution for the preparation of a series of more coarse-grained sols.

In the calculation, spherical shape of the particles was as-

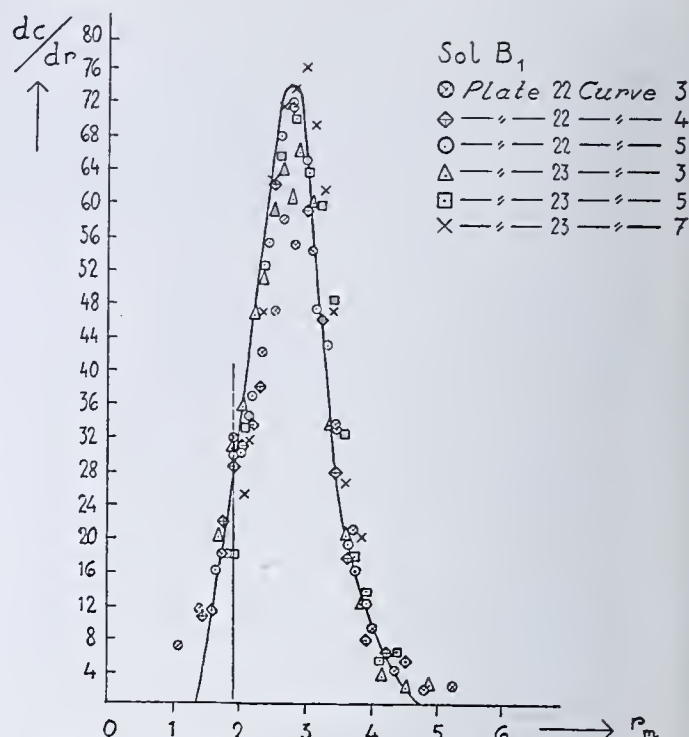


FIGURE 28. SIZE-DISTRIBUTION CURVE OF A FINE-GRAINED GOLD SOL REDUCED BY PHOSPHORUS (RINDE)

sumed and the charge effect neglected (some correction for this latter effect is probably needed, thus giving a slightly larger value for  $r$ ). By depositing gold on the particles of this sol in four consecutive steps a new sol, the distribution of which is given in Figure 29, was obtained. The curve indicates the size distribution which one would expect if the gold nuclei grow as crystals in a supersaturated solution.

Detailed studies on the formation and properties of ferric oxide sols were performed by Bailey, Nichols, and Kraemer (3). Figure 30 shows the effect of concentration during hydrolysis on the distribution curve of the sol.

### Utilization of Ultracentrifuge

The utilization of the ultracentrifuge for the study of high-molecular compounds is only beginning. As research goes on new problems present themselves for treatment with this new tool. So far the main interest of applications has been in the field of biology and medicine because of the various

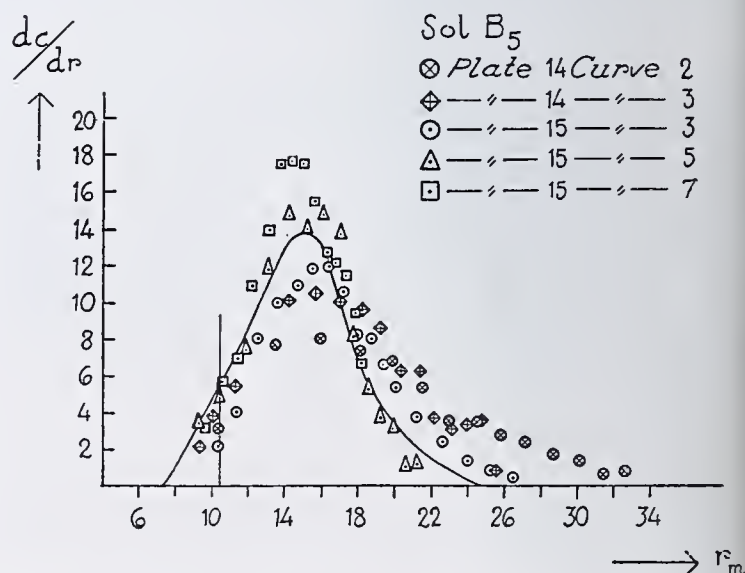


FIGURE 29. SIZE-DISTRIBUTION CURVE OF A GOLD SOL (RINDE)

Obtained by depositing gold on particles of a fine-grained sol



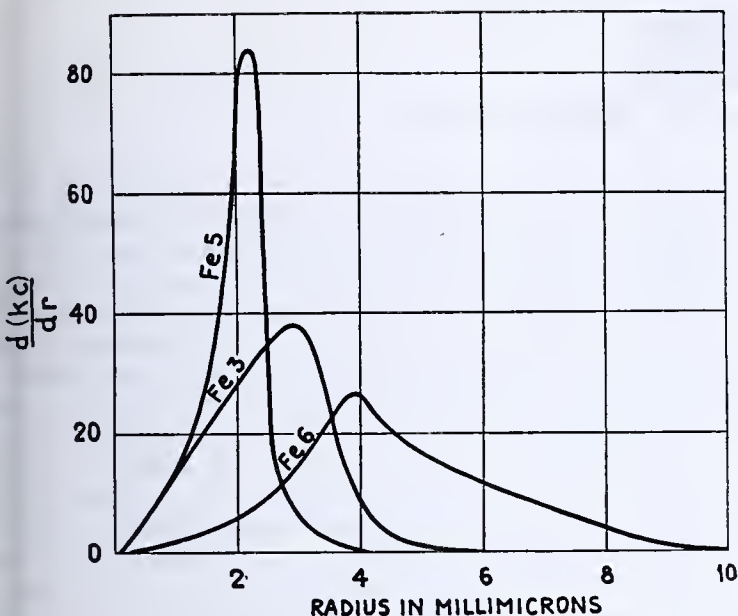


FIGURE 30. EFFECT OF CONCENTRATION DURING HYDROLYSIS ON DISTRIBUTION CURVE OF FERRIC OXIDE (BAILEY, NICHOLS, AND KRAEMER)

Fe 5, 0.003 M  $\text{FeCl}_3$ ; Fe 3, 0.005 M  $\text{FeCl}_3$ ; Fe 6, 0.037 M  $\text{FeCl}_3$

kinds of new information which the ultracentrifuge has made available with regard to the behavior of the proteins, those substances of paramount importance to all living beings. But there are also the vast fields of the carbohydrates, the hydrocarbons, and the synthetic organic high-molecular compounds. A number of important chemical industries are handling stuffs belonging to one or the other of these classes of substances. The research laboratories connected with such industries are beginning to realize that the ultracentrifuge may be able to render services of great value in elucidating the properties of the molecules and particles which are the building stones of cellulose, artificial silk, varnishes, rubber, dyes, and many other products, thus helping us to gain information about many of the native and artificial macromolecular systems which are now in the center of technical interest.

Apparently there is a growing interest in ultracentrifugal studies and we may hope for a rapid accumulation of data useful in the elucidation of the structure of high-molecular substances.

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## Discussion

ELMER O. KRAEMER

E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

AS PROFESSOR Svedberg has in effect pointed out, a complete ultracentrifuge laboratory should possess facilities for studying solutions and suspensions at centrifugal forces from a few times gravity up to the highest attainable centrifugal forces. To cover such a wide range, Professor Svedberg has found it practical to employ two machines, one using a direct-connected commercial electric motor for driving the rotor at speeds up to 18,000 to 20,000 r. p. m.; the other being his famous oil-turbine machine which operates at the highest attainable speeds. As is well known, the oil-turbine ultracentrifuge is a rather formidable machine, and very few institutions can afford to install it. Owing to the publicity that the high-speed machine has received, there is a widespread impression that ultracentrifuge research is out of the question for the average chemical laboratory. This is by no means the case, for a wide variety of problems can be successfully attacked with the low-speed ultracentrifuge. The low-speed machine is relatively simple in construction and operation and of course is much less expensive than the high-speed one. The possibilities of the low-speed machine may be illustrated by some examples from researches carried out at the du Pont Experimental Station.

Using the sedimentation equilibrium method, we have studied in considerable detail the molecular weight and state of aggregation in solution of a number of long-chain, high-molecular-weight materials, particularly synthetic polyhydroxydecanoic acid, cellulose, cellulose derivatives, rubber, and neoprene and have established the correlation between viscosity and molecular weight for such long-chain molecules. In contrast with the proteins about which Professor Svedberg has told you, all these materials are mixtures of molecules of many sizes, and a theory has been developed for quantitatively describing the degree of nonuniformity of these high polymers from sedimentation equilibrium data. This method, we feel, is at the present time the most satisfactory for measuring nonuniformity of materials showing marked diffusivity.

The low-speed machine is not limited to the study of high polymers, and under favorable conditions molecular weights less than 2000 may be measured. Thus, a brief study was made of sodium eosinate and sodium erythrosinate, from which it was concluded that these dyes were associated in solution as double molecules. In this case, the high density of the dye molecules permitted study at relatively low centrifugal forces. In other cases, small molecules may be successfully studied with the low-speed machine and high density solvents.

Another distinct field for the low-speed machine is in the determination of the particle-size distributions of finely divided materials extending from the finest of inorganic colloids up to particles large enough to classify by sieve methods or measure by microscopic means. In all these cases, the diffusivity is so low that a direct determination of size distribution is possible from sedimentation velocity data. The first published papers on the ultracentrifuge dealt with this type of work and gave results for materials such as colloidal gold and arsenic trisulfide, clays, and pigments. The methods are applicable to fine powders of any kind, which can be suspended in a liquid, and the data are of obvious importance whenever the particle size is an important variable in determining the utility and merit of the powdered material.

Out of the study of white powders has developed an understanding of the laws relating particle size and light-scattering efficiency. This arose because of the fact that the progress of ultracentrifuging is followed by optical means; specifically the changes in concentration in the centrifuge cell are recorded in terms of light absorption. Now, since the light absorption of suspensions varies with the particle size, a true particle-size distribution cannot be directly obtained from the ultracentrifuge data.

It was therefore necessary, in order to determine true size distributions, to derive from the ultracentrifuge data the relationship between particle size and light absorption, for it is impossible to prepare samples of fine powders so homogeneous as to permit a direct measurement of particle size and absorption coefficient. By means of a mechanical product-integral this problem was solved. The results elucidate such varied questions as the opaqueness of fogs; the covering power of pigments in paper, paints, and lacquers; the transmission of opal glass; and numerous others which involve the optical properties of turbid systems.

The same methods may be applied to the study of emulsions, using the low-speed machine, and in our publications it is shown how the mechanism of emulsification can be elucidated. In this connection it was found that the particle size of neoprene latex is extraordinarily small and uniform, compared to emulsions of ordinary oils in water stabilized with conventional emulsifying agents. Closer examination of the neoprene latices revealed the fact that self-emulsification occurs at a certain stage in the polymerization of the chloroprene, probably owing to the heat of polymerization.

In another study, the optical properties of emulsions were worked out in more detail, and it was found that a single law describes the interrelationship of light absorption of the emulsion with the concentration and particle size of the emulsified oil, the refractive indices of the oil and the suspension medium, and the wave length of light.

As another line of study, we may mention the hydrous oxides of the metals and metalloids. Depending upon the concentration and the presence of electrolytes, the condition of the solute in solutions of the alkali silicates, stannates, tungstates, molybdates, manganese, metals of the iron group, aluminum, and many others, is intermediate between that of well-defined colloid suspensions and true solutions of single molecules. In many of these cases, the low-speed centrifuge provides the best method of determining the conditions of the solution. We have studied in some detail in this way the mechanism of formation of hydrous ferric oxide from ferric chloride, and the same methods could be applied to any number of these systems.

These examples should suffice to indicate the wide applicability of the low-speed ultracentrifuge to problems of industrial importance, as well as of purely scientific interest. In fact, in view of the simplicity of the equipment and its operation, I feel that any university making a pretense at doing thorough work in colloids should by all means possess a low-speed ultracentrifuge even though it cannot finance an oil-turbine machine. In former years the first piece of equipment installed in a new colloid laboratory was an ultramicroscope, but today, it should be an ultracentrifuge.



## Discussion

HUGH S. TAYLOR, Princeton University, Princeton, N. J.

THE choice of Professor Svedberg to give an exposition of his contributions to physical chemistry at the dedication of the Chemistry Building of the University of Delaware has permitted us a glimpse into the potentialities of a rapidly developing region of experimental research. Every invention or development of a new method of physical measurement enlarges the horizons of the sciences. That is particularly true in the subject to which our lecturer has addressed himself. The instruments which he has developed have made possible powerful new methods of approach to problems that the scientist earnestly desires to solve. We have been shown how these new techniques are applicable to the more complex forms of matter, forms which originate in vital systems and which are being synthesized in increasing degrees in the laboratories and factories of the world. The complexity of these systems, the great size of the individual units or molecules of which these materials are composed has, hitherto, rendered the problem of their investigation a most difficult one.

Researches in the field of synthetic organic chemistry, notably in the synthesis of natural dyes and of similar but improved derivatives, the synthesis of sugars, of vitamins and hormones, are among the brilliant chapters of organic chemistry. Nevertheless, unaided organic chemistry has not appeared capable of carrying the synthesis of the more complex natural products, such as proteins, very far beyond the pioneering researches of Emil Fischer. To this problem the technic discussed today brings a vital contribution.

Professor Svedberg's centrifuge permits a determination of unit molecular size with a precision that is truly remarkable. It permits a differentiation or determination of size distribution in groups of natural and synthetic products where heterogeneity obtains. Upon the firm basis of these unit mass determinations, science in many of its branches is preparing to push forward its horizons. Professor Svedberg's work is invaluable in the field of biochemical investigations where already techniques have been developed to produce protein materials in crystallizable forms. Researches such as those of Northrop on pepsin and trypsin, of Sumner, of Stanley on the mosaic viruses of the tobacco plant—these represent achievements where the assistance of the supercentrifuge is evident and important for further progress. The unitary characteristics of these materials have been recognized and upon that as a foundation we may expect a development similar to that which occurred in inorganic and organic chemistry in the early part of the 19th century when the concept of atomic and molecular structure had been properly defined. Already

there are signs that such a super structure of further discovery is being erected.

In our own field of reaction kinetics, attention is centering at the moment on the velocities of processes occurring among such complex systems. With our newly acquired knowledge of the unitary structure it has become possible to study more intimately processes of change, such as denaturation, of which the speeds can be measured. At the moment, there are surprising differences between the velocities of some of these biochemical processes and the type reaction velocities of classical physical chemistry. Investigators such as Pauling and Mirsky in California, Eyring in Princeton, and Steinhardt in Copenhagen, are concerning themselves with the problem of protein reaction velocities which occur very much more rapidly and with considerably higher temperature coefficients than are possible in the reactions of simpler molecules, whether inorganic or organic.

Recent discussions of the velocity of certain of these processes indicate that they may proceed at velocities which can only be expressed in astronomical figures. I refer more particularly to two reactions recently studied which appear to proceed at velocities  $10^{72}$  and  $10^{26}$  times greater than might be expected. Students of reaction kinetics will ultimately solve these problems. The answer will be found in the pattern of the protein molecule and the count of the individual active groups in the unit molecule which Svedberg has described.

Another approach to the definition of the Svedberg units of complex matter is coming in the field of mathematics. That special branch of mathematics which deals with the subjects of topology has been shown by Dorothy Wrinch to be a very suggestive method of approach to the problem of the structure of the protein molecule. More especially is this the case with those globular proteins which Svedberg has shown to possess such different and discrete levels of molecular weight. These topographical approaches have also inspired a program of synthetic organic chemical research and have stimulated once more the brilliance of Langmuir to further researches on the properties of mono-layers on liquid and now on solid surfaces.

These contributions originating in or aided by a series of researches, cannot be other than inspiring to those fortunate younger generations who will pass through these laboratories of chemical science to the borderlands of scientific knowledge where they may with increasing opportunity and in increasing measure find the happiness and satisfaction of a life dedicated to scientific research.



*Courtesy, Yonkers Public Library*



# Potentiometric Titration in Nonaqueous Solutions

## Solvents

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THE successful use of the alcohols as titration media has permitted the direct determination of acidity of various materials not soluble in water. Ethyl alcohol (3), *n*-butyl alcohol (6), and amyl alcohol (5) have all been used, the latter two in the virtual absence of water. The present work was undertaken in an attempt to utilize the solvent properties of the ethylene glycol monoalkyl ethers (Cellosolves) and other

the most widely used solvents for numerous organic compounds and mixtures. [Dioxane, as well as numerous other solvents, was rejected recently (4) for potentiometric titration because of its low conductivity and low solvent power for oxidized oils. The conditions in this case, however, were different than the present one.]

## Apparatus

The apparatus used consisted of a Leeds & Northrup Type K potentiometer and 2500- $\epsilon$  galvanometer, a saturated calomel half-cell, a quinhydrone electrode, a titration cell, and a storage system for alkali (1, 7). Titrations have also been carried out with the thermionic titrimeter (1).

## Reagents

**SOLVENTS.** The ethylene glycol monomethyl ether was purified by treating the commercial product as follows: Add 30 grams of animal charcoal to 4 liters of the solvent, stir, and filter. Add an additional 30 grams of the charcoal and 500 grams of anhydrous sodium sulfate. Allow to stand overnight, add 20 grams of sodium wire, and distill *in vacuo* at a temperature of 75° C.

The other solvents were obtainable commercially in a relatively pure state.

**ALKALI SOLUTION.** A 0.05 *N* solution of potassium hydroxide in the purified ether, prepared and stored as with butyl alcohol solutions, was used as a standard reagent for the titrations in this solvent. The stability of such a solution is comparable to that of similar butyl alcohol solutions (?). The sodium butoxide in butyl alcohol used in part of the work was prepared and stored as previously described (?).

**LITHIUM CHLORIDE SOLUTIONS.** Lithium chloride (c. p.) was dissolved in the purified solvent (or in *n*-butyl alcohol) by refluxing 200 grams of the salt with 1 liter of solvent.

**ACIDS.** The acids used were of c. p. quality with the exception of the benzoic acid, which was Bureau of Standards material and was used for standardization of the reagent.

**BLANK ON REAGENTS.** The blank titration on 100 cc. of solvent containing 50 mg. of quinhydrone usually was found to be 0.05 cc. or less of 0.05 *N* reagent.

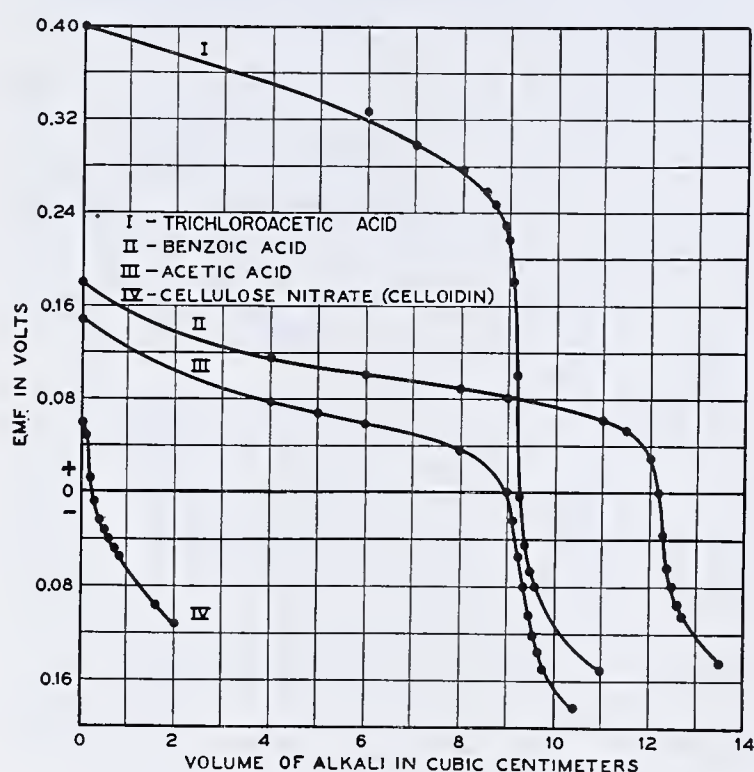


FIGURE 1. TITRATIONS IN ETHYLENE GLYCOL MONOMETHYL ETHER

solvents in acidity determinations for substances not appreciably soluble in the alcohols already studied. Many titrations were performed with solutions in the monomethyl ether (methyl Cellosolve); a few were tried in the monoethyl ether with equal success; the higher ethers have not been investigated but ought to offer no difficulties, should their solvent properties prove especially desirable.

In addition to the pure solvent system employing methyl Cellosolve, several mixed systems have been used with success. In these cases acetone, anisol ( $C_6H_5 \cdot O \cdot CH_3$ ), and 1,4-dioxane ( $C_4H_8O_2$ ) have each been used to enhance the solvent action of *n*-butyl alcohol. The *n*-butyl alcohol is apparently necessary to ensure normal behavior of the quinhydrone electrode. Each of these diluents has solvent properties not exhibited by butyl alcohol. Thus, anisol is an excellent solvent for asphalts and pitches (2), dioxane readily dissolves the heavier oils, while acetone is one of

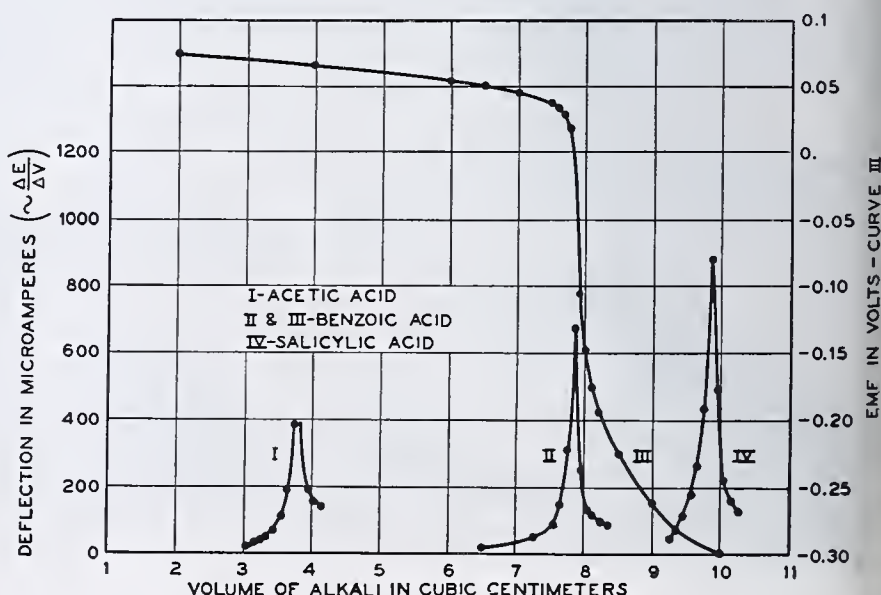


FIGURE 2. TITRATIONS IN ACETONE-BUTYL ALCOHOL



## Experimental

**ETHYLENE GLYCOL MONOMETHYL ETHER.** Solutions of benzoic, trichloroacetic, and acetic acids were prepared approximately 0.05 *N* in strength. Ten cubic centimeter aliquots were titrated in 100-cc. volumes of solvent to each of which 10-cc. portions of the lithium chloride solution had been added. Sharp end points were obtained (Figure 1), and the titrations were characterized by steady potentials and rapid assumption of equilibrium after each addition of reagent.

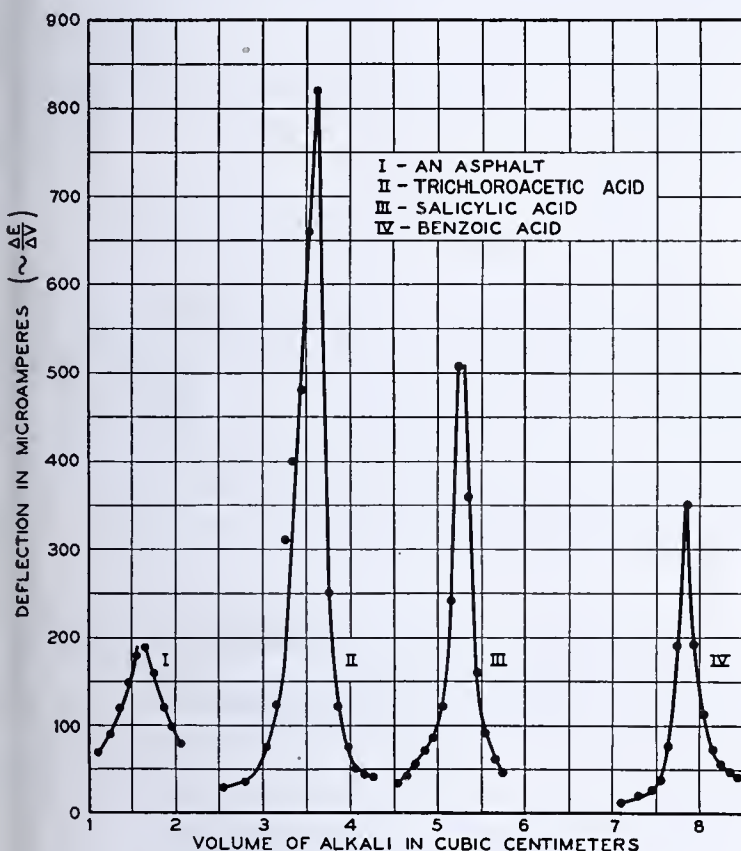


FIGURE 3. TITRATIONS IN ANISOL-BUTYL ALCOHOL

Samples of cellulose nitrate and of cellulose acetate were also titrated. These materials are readily soluble in the glycol ethers and do not interfere with the proper functioning of the quinhydrone electrode. Aliquots of acetic acid added to solutions containing cellulose acetate were completely titrated, showing the feasibility of acidity determinations of weak acids in this solvent.

**ACETONE-BUTYL ALCOHOL.** For practical purposes it is useful to employ sodium butoxide in butyl alcohol as the reagent (7), especially if it is in constant use for other purposes in the same laboratory. Also it is advantageous to add 10 cc. of a saturated solution of lithium chloride in butyl alcohol to each 100 cc. of acetone before titration, especially if a potentiometer is to be used. Titrations of benzoic acid, acetic acid, and salicylic acid, using the quinhydrone electrode as the indicator are shown in Figure 2. The titers were the same as those obtained in butyl alcohol solution, using the same reagent.

**ANISOL-BUTYL ALCOHOL.** Pure anisol is unsatisfactory as a medium for the quinhydrone electrode, because of apparent instability of the quinhydrone as the end point is approached. The instability is characterized by the appearance of a blue-green color and by drifting potentials. When sufficient butyl alcohol is present the quinhydrone electrode behaves normally and the solvent powers of anisol for asphalts and pitches are not seriously impaired. Titrations of several acids and of a typical asphalt are shown in Figure 3.

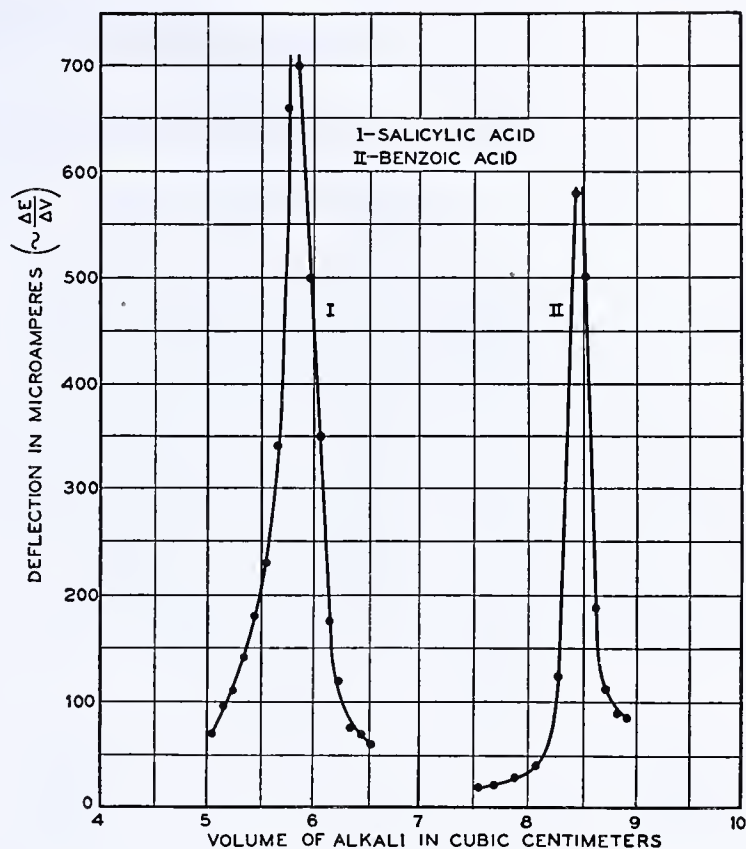


FIGURE 4. TITRATIONS IN 1,4-DIOXANE-BUTYL ALCOHOL

**DIOXANE-BUTYL ALCOHOL.** The same instability of the quinhydrone electrode as was encountered in anisol solutions was also found with dioxane, but in this case too it disappeared when the solvent was mixed with butyl alcohol. Titration curves in this mixture are shown in Figure 4.

## Summary

Use has been made of the monomethyl ether of ethylene glycol as a medium for the potentiometric determination of acidity of materials soluble in this solvent.

Acetone, anisol, or 1,4-dioxane can be used to enhance the solvent powers of butyl alcohol without interfering with the functioning of the quinhydrone electrode in this solvent. This extends the possibilities of acidity determination to materials soluble in such solvent mixtures.

## Acknowledgment

The author wishes to thank L. A. Wooten for his helpful criticism and advice in this work.

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# Analysis of Maple Products

## Composition of the Canadian Lead Precipitate of Maple Sirup

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**D**ETERMINATIONS published by Fowler and Snell in 1929 (4) of total lead, basic lead, carbon, hydrogen, acid equivalents, and malic acid (polarimetric) in the precipitate produced in the Canadian lead method of analysis of maple sirup (2) showed that while the sum of the lead malate (equivalent to 97 per cent of the organic acids) and the lead oxide accounts for some 84 per cent of the precipitate, the carbon of the malate amounts to little over half that found by combustion, thus indicating the presence of some highly carbonaceous constituent or constituents. The present paper reports a qualitative search for the organic constituents of the precipitate. The quantitative data included in this paper are to be regarded merely as rough approximations.

### Experimental

**ELEMENTARY ANALYSIS.** As the work by Fowler and Snell left open the possibility of the presence of nitrogen, or sulfur, determinations of lead, carbon, and nitrogen, and qualitative tests for sulfur were made in the precipitates from three sirups. The results are given in Table I. The percentages of carbon (by combustion) and of lead (weighed as chromate) are similar to those previously reported (4, 11). The Kjeldahl process revealed only a trace of nitrogen, and a sodium fusion method not even a trace of sulfur when tested with nitroprusside.

TABLE I. ELEMENTARY ANALYSIS OF CANADIAN LEAD PRECIPITATES OF THREE MAPLE SIRUPS

	Sirup 1	Sirup 2	Sirup 3
Canadian lead number	2.66	3.15	3.93
Total lead, per cent	68.08	68.90	69.30
Carbon, per cent	11.55	11.65	12.05
Nitrogen	Trace	Trace	Trace
Sulfur	None	None	None

**PREPARATION OF PRECIPITATE IN QUANTITY.** Two imperial gallons of sirup (Canadian lead number 3.93), obtained from Les

Producteurs de Sucre d'Erable de Quebec, were diluted to concentration of 25 per cent sucrose, treated with 3050 ml. of basic lead acetate reagent, and allowed to settle 2 hours. The supernatant liquid was siphoned off and the precipitate washed three times with 6-liter portions of water. The precipitate was then transferred to a Büchner filter, washed several times, dried at 100° C., and weighed; the yield of 300 grams was approximately that to be expected from sirup of Canadian lead value 3.93, the process being as close an approximation as practicable to that used analytically.

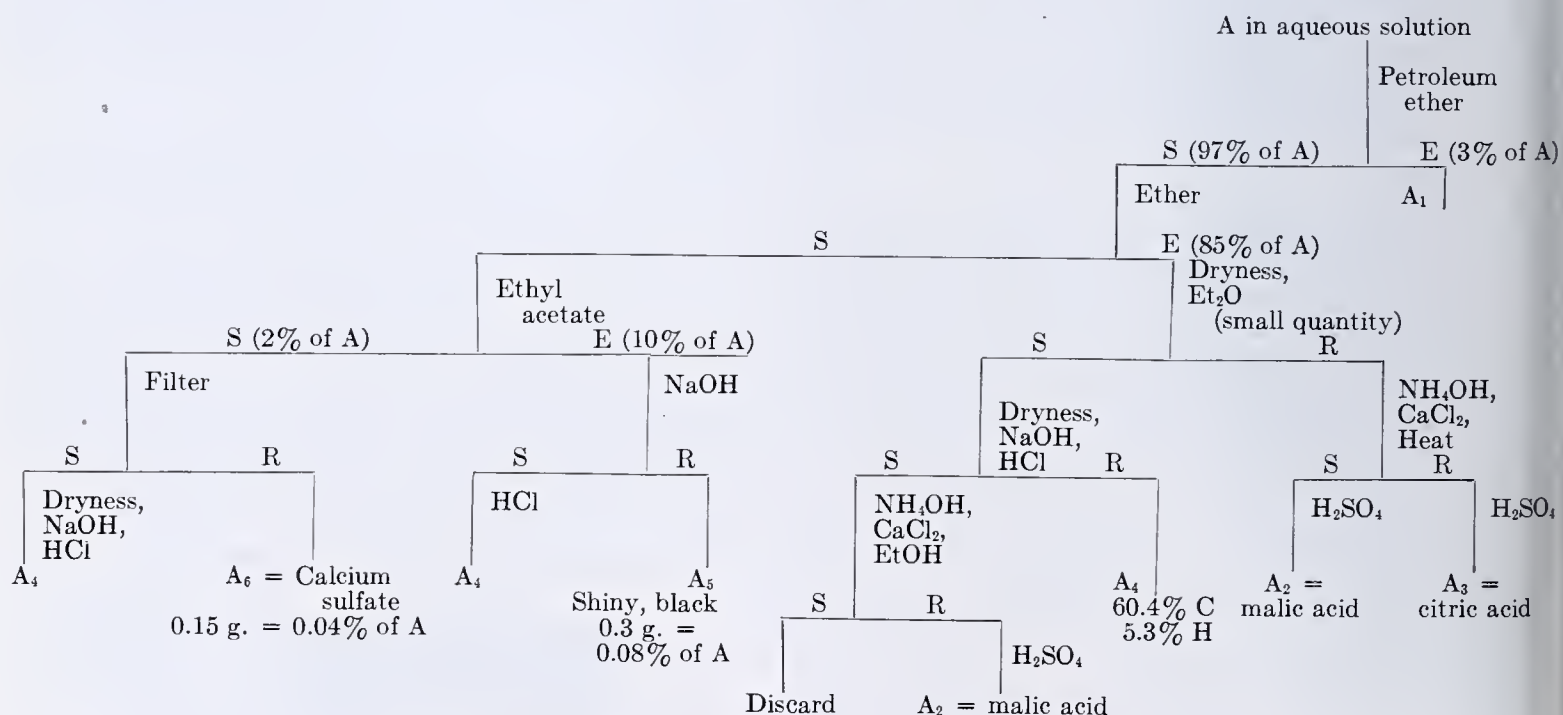
2 gallons of sirup = 26.4 pounds = 11,975 grams

Solids = 65 per cent = 7784 grams

Lead precipitate, 3.93 grams per 100 grams solids = 306 grams

**REMOVAL OF THE LEAD.** Two hundred grams of the precipitate suspended in water were treated with hydrogen sulfide for 24 hours with mechanical stirring, filtered, and washed. The precipitate was found to contain 4.4 per cent of carbon; it was therefore given a second treatment with hydrogen sulfide for 12 hours with alternate heating to boiling and cooling, and again filtered and washed. Carbon (2.5 per cent) being still present, the precipitate was refluxed with a slight excess of 2 *N* sulfuric acid. Being now practically free from carbon, the precipitate was discarded. The filtrates from the three treatments were designated fractions A, B, and C, respectively.

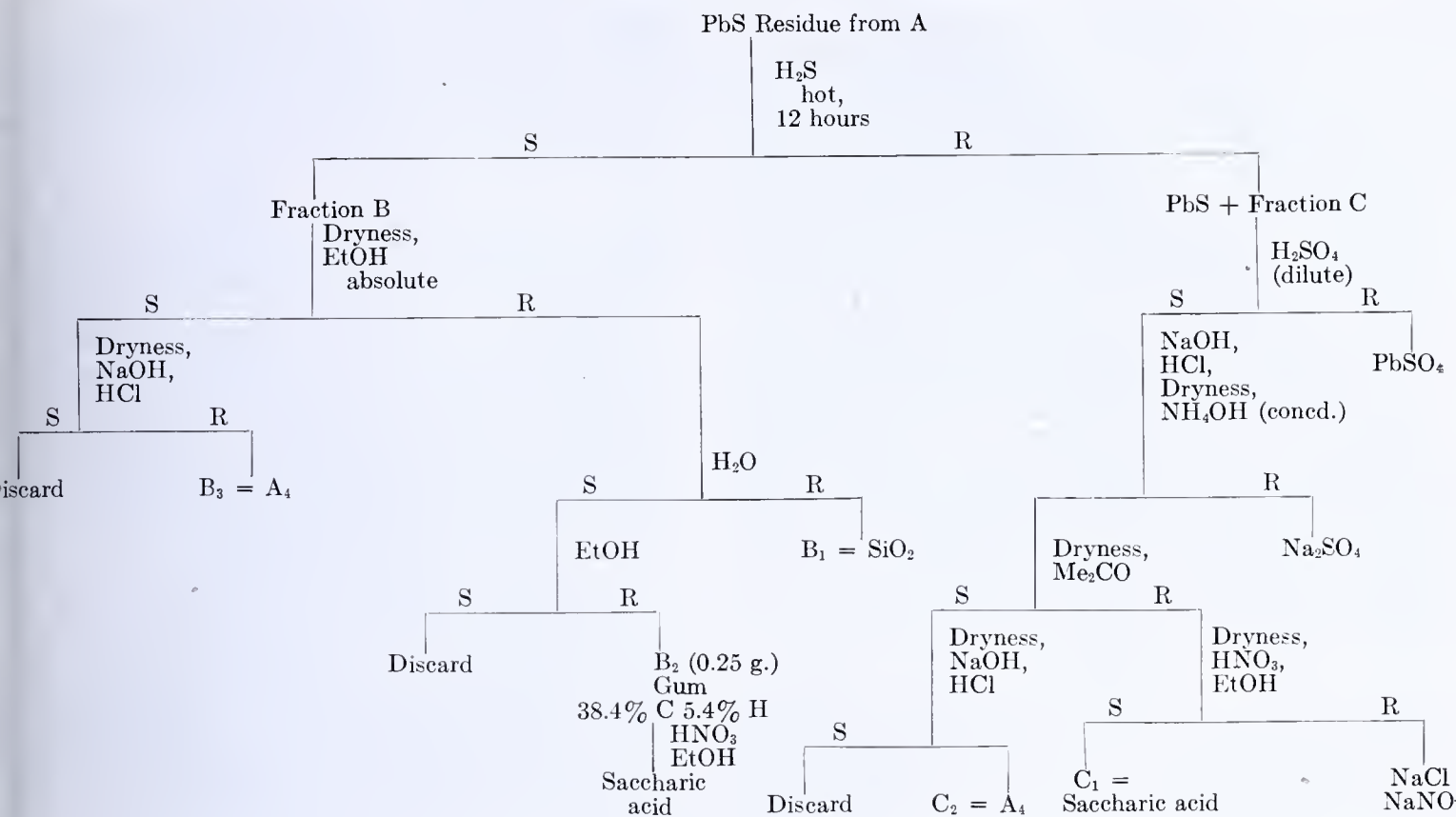
**TREATMENT OF FRACTION A (FLOWSHEET 1).** Fraction A was concentrated under reduced pressure from an original volume of about 4 liters to 100 ml. and further to dryness in a vacuum desiccator. The light-brown deliquescent residue, weighing about 45 grams, dissolved completely in absolute alcohol, indicating absence of pectin (9, p. 128). The solution reduced Fehling's reagent, gave a precipitate with bromine water, and blackened on exposure to air. It gave no precipitate with gelatin. Diluted with water and treated with ferric chloride, it gave a distinct green color. A test with goldbeater's skin and ferrous sulfate (8) gave a negative result.



FLOWSHEET 1. SEPARATION OF FRACTION A

E = Extract R = Residue S = Solution





FLWSHEET 2. SEPARATION OF FRACTIONS B AND C

R = Residue S = Solution

These results indicate that if tannins are present they belong to the phloba or catechol groups (1). Evidence of the presence of such tannins in fractions B and C is given below.

The alcohol was distilled off from fraction A, which was then redissolved in water and fractionated by successive extractions with petroleum ether, ethyl ether, and ethyl acetate as outlined in Flowsheet 1. These three solvents extracted, respectively, about 3, 85, and 10 per cent of fraction A.

The petroleum ether extract ( $A_1$ ) amounted to 1.5 grams of an oily product. Two distillations under reduced pressure yielded about 1 gram of colorless liquid, having a refractive index of 1.4346 at 23° C. It was viscous at -20° and boiled with browning at about 170°. It precipitated basic lead acetate and readily reduced Fehling's solution, ammoniacal silver nitrate, permanganate, and bromine. It did not react with saturated sodium bisulfite nor with semicarbazide, but did yield a 2,4-dinitrophenylhydrazone, melting at 95° C. It was readily soluble in alkalis and was not precipitated from such solutions by carbon dioxide. With ferric chloride a brown coloration was given, and with sodium an evolution of hydrogen. The results indicate a carbonyl compound, probably enolic.

In the ether extract malic acid was identified by conversion into the *p*-nitrobenzyl ester (m. p. 124°) and citric acid by precipitation of the calcium salt and by the color test of Schmalfuss and Keitel with vanillin and sulfuric acid (9, p. 23; 10).

Treatment with ferric chloride after destruction of hydroxy- and unsaturated acids with permanganate, according to the method of Heide and Steiner (5), failed to reveal the presence of succinic acid, though this acid has been reported in maple sap by Findlay and Snell (3) and in the sirup (in small proportion) by Nelson (6). Fumaric acid was detected in traces by hydrogen chloride esterification with methyl alcohol, a few crystals of correct melting point and mixed

melting point being obtained. (The lead precipitate of a molded sirup yielded 1 per cent of methyl fumarate.)

The ethyl acetate extract, which contained acetic acid, formed by hydrolysis of the solvent, contained most of the coloring matter of the precipitate. The color deepened during the extraction, possibly through action of the acetic acid on the tannin. Concentrated *in vacuo* by distillation and finally in a desiccator over solid sodium hydroxide, it yielded about 0.3 gram of a shiny black substance,  $A_5$ , which upon combustion showed 30 per cent carbon, 3.26 per cent hydrogen, and 50 per cent ash.

From both the ether and the ethyl acetate extracts a brown material,  $A_4$ , was obtained by acidification of alkaline solutions with dilute hydrochloric acid. The same material appeared in fractions B and C. The extracted aqueous layer contained some organic matter which was separated from the sodium chloride by evaporation to dryness and extraction with acetone. Upon evaporation the acetone solution yielded a colorless bitter residue, which darkened on exposure to air and lost its bitter taste.

**TREATMENT OF FRACTION B (FLWSHEET 2).** Concentrated to 50 ml. by vacuum distillation and to dryness in a vacuum desiccator over sulfuric acid, fraction B yielded a residue only partly soluble in absolute alcohol. The soluble portion contained the brown material,  $A_4$ . The insoluble portion yielded silica and about 0.25 gram of  $B_2$ , glossy plates browning at 195°, decomposing at 210°, and containing, according to a single combustion, 38.1 per cent carbon and 5.4 per cent hydrogen. It responded to Molisch's test and was precipitated from aqueous solution by basic, though not by neutral, lead acetate. It did not reduce Fehling's solution but was readily hydrolyzed to a reducing sugar. On treatment with nitric acid (sp. gr. 1.15) it yielded saccharic acid. It would appear to be a gum.

**TREATMENT OF FRACTION C (FLWSHEET 2).** Before vacuum distillation, this fraction was neutralized with sodium hydroxide and acidified with hydrochloric acid. The



excess of hydrogen chloride was removed by triple evaporation with alcohol. The residue was treated with four successive 50-ml. portions of ammonium hydroxide to dissolve the organic matter. This treatment excluded the sodium sulfate. A good deal of the sodium chloride crystallized out during concentration of the ammoniacal solution.

The sulfuric acid treatment of the lead precipitate had no doubt hydrolyzed the gum found in fraction *B* to alcohol-soluble products. These treated with nitric acid yielded saccharic acid.

The brown substance, *C*<sub>2</sub>, was apparently identical with *A*<sub>4</sub> and *B*<sub>3</sub>. In all, about 3 grams of this material were obtained. It was found to contain 60.4 per cent of carbon and 5.28 per cent of hydrogen. It decomposed without melting, darkened upon exposure to air or to acid vapors, and was only slightly soluble in cold water but readily soluble in alkaline solutions and in alcohol. Its alcoholic solutions imparted a green color to ferric chloride. A test tube distillation with zinc dust at 330° C. yielded a brown substance with the odor of anthracene. All this behavior is consistent with the conjecture that the brown substance is a phlobaphene (1, 7, 9).

### Summary

By treatment with hydrogen sulfide, cold and hot, and with dilute sulfuric acid, the precipitate produced from maple sirup by treatment with basic lead acetate was separated into

fractions *A*, *B*, and *C*. Fraction *A* yielded malic and citric acids and an oily liquid yielding a 2,4-dinitrophenylhydrazon of m. p. 95° C. A carbohydrate gum was detected in fraction *B* and its hydrolysis product in fraction *C*. Phlobatannins were indicated in all three fractions.

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# Rapid Colorimetric Determination of Lead in Maple Sirup

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THE colorimetric method described has been developed primarily to facilitate the analysis of sirups for lead content during the short harvest season and to provide a rapid sorting test which could be employed in field stations. Results obtained during preliminary work indicate an accuracy to within 0.001 grain per pound (0.143 p. p. m.) and good adaptability to routine laboratory work. Checking by a longer and more accurate method (2) would seem necessary only in isolated cases. The method is similar to the procedure (1) employed for several years to estimate spray-residue lead on fruit, particularly apples. Its accuracy depends largely upon the ability of the analyst to distinguish small differences in color tints. With a fair amount of practice in matching the colors involved, little difficulty should be experienced in obtaining good results.

### Principles

The index of the lead content of the sirup is the amount of red lead-dithizone complex produced when a solution of diphenylthiocarbazone (dithizone) in chloroform is shaken with the ammoniacal sample solution. The dithizone solution, normally green in color, gives color changes dependent upon the proportion of the reagent which is changed to the red complex (PbD<sub>2</sub>) by the lead present. Increasing amounts of lead produce changes from the original green through a series of intermediate blues and purples to a cherry red when all the dithizone is in combination. These colors are readily matched against colors produced from known amounts of lead in solution under identical conditions.

### Reagents

All reagents should be as free from lead as possible.

1. HYDROCHLORIC ACID, approximately 35 per cent HCl. Dilute 180 cc. to 1 liter with distilled water.
2. AMMONIA-CYANIDE-CITRATE REAGENT. Dissolve 20 grams of potassium cyanide and 10 grams of citric acid in 500 cc. of ammonium hydroxide (approximately 28 per cent NH<sub>3</sub>) and dilute to 1 liter. Preserve in a manner to minimize loss of NH<sub>3</sub>.
3. DIPHENYLTHIOCARBAZONE (DITHIZONE). This reagent must be purified according to the A. O. A. C. methods or equivalent. Dissolve 30 mg. in 1 liter of chloroform (a) and dilute a portion of this solution with an equal volume of chloroform to give a solution containing 15 mg. per liter (b). These solutions should be kept in a cool dark place when not in use.
4. STANDARD LEAD SOLUTION. Pure lead nitrate, twice recrystallized and dried to constant weight at 100° to 110° C., should be used. A stock solution containing 10 mg. per cc. of lead in about 0.1 per cent nitric acid can be prepared and further dilutions made as needed. Lead tends to precipitate (probably as silicate) from very dilute solutions in the absence of acid. Prepare the standard solution in hydrochloric acid (reagent 1) to contain 3.864 mg. per liter of lead.

### Standards

Introduce into each of ten 50-cc. tall-form Nessler tubes the quantities of blank acid (reagent 1) and standard lead solution (reagent 4) indicated in Table I. Since the total quantity of each solution used is 50 cc., the buret readings are given for convenience.

Add to each tube 10 cc. of ammonia-cyanide-citrate reagent and 10 cc. of dithizone solution (3b) accurately measured.



TABLE I. PREPARATION OF STANDARDS

Lead Grain/lb. <sup>a</sup>	Standard Used Cc.	Buret Reading Cc.	Blank Used Cc.	Buret Reading Cc.
0.000	0.0	0.0	10.0	10.0
0.003	1.1	1.1	8.9	18.9
0.006	2.2	3.3	7.8	26.7
0.009	3.4	6.7	6.6	33.3
0.012	4.4	11.1	5.6	38.9
0.015	5.5	16.6	4.5	43.4
0.018	6.7	23.3	3.3	46.7
0.021	7.8	31.1	2.2	48.9
0.024	8.9	40.0	1.1	50.0
0.027	10.0	50.0	0.0	0.0

<sup>a</sup>  $\approx$  143 p. p. m.

shake the tubes vigorously (35 to 50 times) and allow the layers to separate. The standard tubes should be kept in a dark place when not in use and should be freshly prepared daily.

### Determination

Weigh 15 grams of sirup into a clean 100- to 125-cc. (4-ounce) sample bottle or other tube suitable for centrifuging, add 15 cc. of acid reagent 1, and mix well. Add 15 to 25 cc. of water, 15 cc. of ammonia-cyanide-citrate reagent, and exactly 15 cc. of strong dithizone solution (3a). Shake vigorously (100 to 200 times) and whirl in a centrifuge to separate the layers. Transfer exactly 11 cc. of the dithizone layer with a pipet to a 100-cc. separatory funnel containing 11 cc. of the acid reagent. To remove the chloroform-dithizone mixture, place the finger on the pipet before immersion in the liquid and allow the tip to come in contact with the bottom of the tube before removing the finger. Draw the mixture above the 11-cc. mark, remove the tube, and wipe the pipet tip with a clean cloth before adjusting to the mark. Shake the funnel vigorously (200 times), releasing the pressure several times, allow the layers to separate cleanly, and draw off the chloroform-dithizone mixture from which the chloroform can be reclaimed later. Pipet 10 cc. of the aqueous acid layer into a test tube, add 10 cc. each of ammonia-cyanide-citrate and weak dithizone (3b) solutions, stopper, and shake vigorously. Allow the layers to separate and compare the dithizone colors with the standards in a comparator block.

When the sample contains more than 0.027 grain per pound of lead, use a 5-cc. aliquot with 5 cc. of blank acid and multiply the result by 2. If more than 0.050 grain per pound is present, it is advisable to use 30 cc. of strong dithizone as in the initial extraction and a 5-cc. aliquot as above and multiply the results by 4. For amounts of more than 0.100 grain per pound use a smaller initial sample.

Make a blank determination for the reagents in the above manner, substituting 15 cc. of water for the sirup.

Make color comparisons with a tube of clear chloroform backing the sample tube and tubes of chloroform which have been shaken with blank acid and ammonia-cyanide-citrate solutions backing two standard tubes on both sides of the sample tube. Use a comparator block allowing the minimum space between tubes with a uniform light source. The use of artificial light in conjunction with a Corning ground-glass daylight filter is satisfactory. View the colors at right angles to the tube lengths. Since the standards are made up in intervals corresponding to 0.003 grain per pound, it is necessary to interpolate when reading the sample tube. This can be conveniently done to within 0.001 grain per pound (grain per pound  $\times$  143 = p. p. m.).

### Discussion and Notes

No interferences from metals ordinarily present in maple products were encountered in this method. Tin and zinc contamination from the tin-plated and galvanized maple-producing equipment is expected. Observations indicate that a contamination from the tin-plated equipment, if present, causes little or no interference. Stannous tin will form a dithizone complex under conditions of the method, while stannic tin will not. Any tin if present is probably in the stannic form. Sap when boiled down to sirup in the presence of a large excess of pure granulated tin tended to lose an appreciable amount of the lead present by electrochemical deposition, but gave no abnormal results upon analysis by

the method outlined, indicating that any tin take-up was noninterfering.

Maple products (3) may contain appreciable quantities of zinc derived mainly from the galvanized equipment. The use of hydrochloric acid in the cold and the double dithizone extraction procedure of the method successfully eliminates interference from this metal. The former use of nitric acid and heat in the preliminary treatment of the sample (2) produced with the sugar present active groups which combined with the cyanide, rendering it ineffective in preventing the formation of zinc dithizone complexes. Lead recoveries in the presence of zinc normally in sirup and recoveries of known amounts of lead added to standard sirups are shown in Table II.

TABLE II. RECOVERY OF ADDED LEAD FROM STANDARD SIRUP

Sample No.	Pb Present Grain/lb.	Zn Present P. p. m.	Pb Added Grain/lb.	Total Pb Recovered Grain/lb.
8A	0.003	30.4	...	0.003
8B	0.025	85.4	...	0.026
8A-1	0.003	30.4	0.003	0.006
8A-2	0.003	30.4	0.009	0.012
8A-3	0.003	30.4	0.015	0.017
8A-4	0.003	30.4	0.022	0.025
Y-1	0.005	...	0.006	0.010
8A-5	0.003	30.4	0.027	0.029
F5044	0.028	300.0	...	0.029

Twenty-seven samples of standard sirup were analyzed for their lead contents by the recent dithizone electrolytic method (2) and by the colorimetric method. The results are compared in Table III.

TABLE III. COMPARISON OF DITHIZONE-ELECTROLYTIC AND DITHIZONE-COLORIMETRIC METHODS FOR LEAD IN MAPLE SIRUP

Sample No.	Lead Found		Sample No.	Lead Found	
	Dithizone- electrolytic	Dithizone- colorimetric		Dithizone- electrolytic	Dithizone- colorimetric
	Grain per pound			Grain per pound	
8-A	0.003	0.003	F5496	0.003	0.003
8-B	0.025	0.026	F7503	0.006	0.006
Y	0.006	0.005	F7885	0.009	0.009
F3173	0.009	0.009	F8000	0.009	0.009
F5495	0.005	0.004	F8304	0.038	0.039
F7959	0.004	0.003	F8306	0.051	0.052
F11220	0.002	0.001	F9151	0.079	0.079
F8305	0.042	0.044	F9152	0.064	0.063
F1549	0.002	0.002	F9160	0.011	0.011
F5011	0.006	0.005	F11225	0.003	0.003
F5044	0.028	0.029	B911	0.015	0.015
F5045	0.013	0.013	B411	0.019	0.019
F5046	0.003	0.003	B919	0.020	0.021
F5073	0.003	0.003			

Glassware which will not add lead to the solutions should be selected. Flint or lead glass should not be used. A good grade of soda-lime or borosilicate glass which has been cleaned with hot strong acid and ammoniacal cyanide solution has been found suitable. An oil sample bottle submitted by Ace Glass Incorporated, Vineland, N. J., was found satisfactory.

### Summary

A rapid colorimetric method for the determination of lead in maple sirup is suggested.

Single samples can be analyzed in about 15 minutes and about 50 samples can be examined daily.

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# Colorimetric Determination of Iron with Salicylic Acid

## A Spectrophotometric Study

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By means of the recording photoelectric spectrophotometer, which provides a method of color measurement entirely objective and capable of high accuracy and precision, a critical study has been made of the colorimetric determination of iron by salicylic acid with particular attention to the effects of diverse ions.

THE reaction between salicylic acid and ferric ion in acetic acid solution to give an amethyst coloration has been known for many years (7, 9, 13), but it was not applied to the quantitative colorimetric determination of iron until 1907 (3). Since then the method has been developed and further applied by many workers (1, 8, 10, 11) and some of its limitations have been indicated. Snell (10) and Yoe (15) report that hydrochloric, nitric, and sulfuric acids, phosphate, thiosulfate, bisulfite, and fluoride interfere, while Sagaidachnui and Ravich (8) say that citrate, tartrate, and oxalate must be absent.

The purpose of the work described in this paper was to make a study of this method by means of the photoelectric recording spectrophotometer (6), with particular attention to the effect of other elements and ions upon the color system. Similar studies of other colorimetric methods have recently been made by Swank and Mellon (12) and by Wright and Mellon (14). If two solutions have the same color under any condition of illumination and to any observer, they will give identical spectral transmission curves. By such curves very small differences in color intensity and in hue can therefore be detected.

### Apparatus and Solutions

All spectrophotometric measurements in the present work were made with the instrument built for the Department of Chemistry of Purdue University by the General Electric Co. (5). All determinations of pH values were made with the glass electrode setup described by Mellon (4).

Standard solutions of iron, each milliliter of which contained 0.1 mg. of iron, were prepared by dissolving weighed amounts of ferrous ammonium sulfate of known iron content in water containing dilute sulfuric acid and by dissolving weighed amounts of iron wire of known purity in dilute hydrochloric acid and in perchloric acid, oxidizing the iron in the first two cases with a few milliliters of 3 per cent hydrogen peroxide and boiling out the excess. The hydrochloric acid solution was used for the tests involving calcium, strontium, and barium ions, the perchloric acid solution for the lead-ion tests, and the oxidized ferrous ammonium sulfate solution for all other tests. Standard solutions of the metals were prepared from the chloride, nitrate, or sulfate salts, while the sodium, potassium, or ammonium salts were used for the preparation of standard solutions of the anions.

The sodium salicylate solution was made by dissolving 10 grams of the salt in 100 ml. of water. Solutions of 1 to 1 acetic acid and 1 to 1 ammonium hydroxide were made by dilution of glacial acetic acid and 15 *M* ammonium hydroxide, respectively. Redistilled water was used for all solutions.

For producing the color system Snell's directions (10) were followed. Five milliliters of the standard iron solution, representing 0.5 mg. of iron, were nearly neutralized by adding 1 to 1 ammonium hydroxide drop by drop. After the addition of 1

ml. of the sodium salicylate reagent, the solution was made slightly alkaline with 1 to 1 ammonium hydroxide and then just acid with 1 to 1 acetic acid added dropwise. Exactly 10 ml. of acetic acid were then added, and the solution was accurately diluted to 100 ml. and thoroughly mixed. The transmittancy curves were determined for a solution thickness of 1.961 cm. The absorption of the glass cell was compensated by placing in the rear beam of light a similar cell filled with distilled water.

### Conformity to Beer's Law

That the color system follows Beer's law, at least up to a concentration of 20 mg. of iron per liter, is apparent from Table I, in which are shown the observed transmittancies at 520  $m\mu$ , the wave length of maximum absorption, for ten iron solutions of different concentrations, together with the transmittancies calculated from the transmittancy of the solution containing 0.1 mg. of iron per 100 ml. The calculations were made by use of the formula which expresses Beer's law

$$T_2 = T_1 \frac{c_2}{c_1}$$

where  $T_1$  represents the observed transmittancy, expressed as a decimal, for the solution of concentration  $c_1$ , and  $T_2$  the calculated transmittancy for the solution of concentration  $c_2$ . The observed and calculated values check very closely.

TABLE I. VALIDITY OF BEER'S LAW

Iron Mg./100 ml.	(pH 2.6 to 2.7; 1.961-cm. cell)	
	Transmittancy at 520 $m\mu$ Observed	Calculated
	%	%
0.1	87.7	...
0.2	77.1	76.9
0.3	67.3	67.4
0.4	58.9	59.1
0.5	51.5	51.8
0.8	34.8	35.0
1.0	27.1	26.9
1.2	20.7	20.7
1.5	14.4	14.0
2.0	7.8	7.3

Further evidence that Beer's law is followed is had by the fact that a straight line results when the logarithm of the observed transmittancy is plotted against the concentration (Figure 1). Although Snell (10) and Yoe (15) state that not more than 1 mg. of iron per 100 ml. should be present when iron is being determined visually, such a limit need not be imposed so far as any lack of conformity to Beer's law is concerned.

### Effect of Reagents

Bech (2), in discussing the photoelectric determination of salicylic acid with ferric chloride, says that a decrease in pH value reduces the color intensity and sets a minimum limit of 2.2. Sagaidachnui and Ravich (8) say that the hydrogen-ion concentration must not exceed 0.01 *N*—that is, the pH value must not be less than 2.0. When prepared by the directions given above, the standard color system has a pH value of 2.6 to 2.7. Presumably it should be possible to buffer the original solution by the addition of ammonium acetate, but such a procedure would involve several determina-



tions of pH value in order to bring the latter within the proper limits.

Table II shows the effect on the color intensity and on the pH value when the volume of acetic acid is varied from 10 ml. The calculations are based upon the solutions containing 10 ml. of acetic acid.

TABLE II. EFFECT OF VARYING VOLUMES OF ACETIC ACID  
(0.5 mg. of iron per 100 ml.; 1.961-cm. cell)

Volume of Acetic Acid ML.	pH	Transmittancy at 520 $m\mu$ %	Apparent Change in Iron Concn. %
15.0	2.4	53.1	-4.4
12.5	2.5	52.4	-2.2
10.0	2.6	51.6	..
7.5	2.7	51.0	+1.8
5.0	2.8	50.7	+2.8

These results indicate that the volume of acetic acid may vary from about 8 to 12 ml. if a 2 per cent error in the iron concentration is allowed as the limit. This limit was chosen in accordance with the procedure of Swank and Mellon (12). The presence of 2 drops of concentrated hydrochloric acid in addition to 10 ml. of acetic acid gave a decrease in color intensity corresponding to an error of 13.2 per cent.

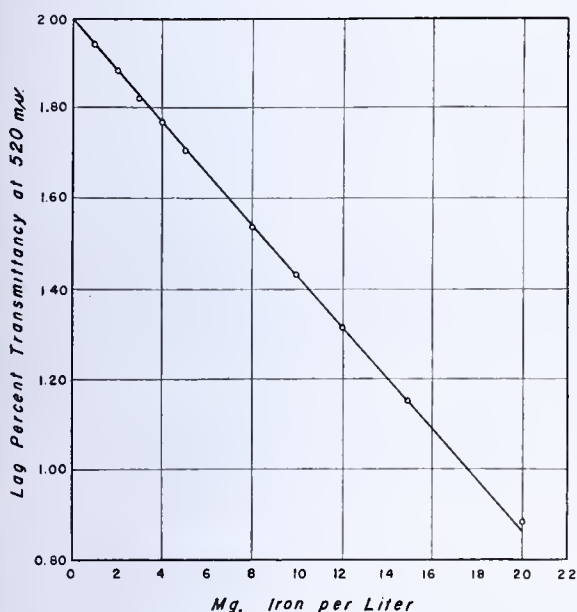


FIGURE 1. CONFORMITY TO BEER'S LAW

Small amounts of nitric and sulfuric acids caused similar decreases in intensity. In actual practice, however, since the solution is almost neutralized with ammonium hydroxide before the salicylate reagent is added, none of these acids will be present in objectionable amounts.

Table III shows the effect when volumes of sodium salicylate solution greater than the specified 1 ml. are used.

TABLE III. EFFECT OF VARYING VOLUMES OF SODIUM SALICYLATE  
(0.5 mg. of iron per 100 ml.; 1.961-cm. cell)

Volume of Salicylate ML.	pH	Transmittancy at 520 $m\mu$ %	Apparent Change in Iron Concn. %
1	2.6	52.0	..
2	3.2	50.2	+5.0
3	3.4	49.4	+8.0
4	3.5	47.7	+13.2

As the volume of salicylate increases a noticeable brownish tint develops. It is evident that not more than 1 ml. should be used unless the volume of acetic acid is increased in order to lower the pH value. The solution of sodium salicylate gives a transmittancy of practically 100 per cent throughout the range of 400 to 700  $m\mu$ , thus showing no absorption.

## Stability of the Color

There is some difference of opinion as to the stability of the color. Yoe (15) states that it fades fairly rapidly in the light, while Snell (10) says it is stable for 48 hours, but fades rapidly in sunlight. Curves were made for four solutions, containing 0.2, 0.5, 0.7, and 1.0 mg. of iron per 100 ml., at intervals after the solutions had stood in glass-stoppered Pyrex bottles in diffuse light under ordinary laboratory conditions. The color was stable within the 2 per cent limit for 66 hours. Exposure to direct sunlight for 6 hours greatly accelerated fading.

## Effect of Anions

In the interference studies the curve produced by the standard iron solution containing 0.5 mg. of iron per 100 ml. was compared with the curve produced by a similar iron solution containing a known amount of the added ion. From the transmittancies at 520  $m\mu$  of the two solutions and the known concentration of the standard iron solution, by use of the formula used above in the Beer's law calculations, the apparent concentration of iron in the solution containing the added ion was calculated. The difference between this value and the actual concentration multiplied by 100 and divided by the actual concentration gave the percentage error. As explained above, a 2 per cent error was arbitrarily set as the maximum allowable for no interference.

A number of the common anions cause a decrease in the color intensity, either through their ability to form colorless complexes with ferric ion which are more stable than the salicylate ferric complex or because they reduce the iron to the ferrous condition. In the former class are tartrate, oxalate, citrate, orthophosphate, pyrophosphate, arsenate, cyanide, tungstate, and fluoride, while in the latter class are sulfite, thiosulfate, and iodide. In Figure 2, curve 3 shows the effect of 1 mg. of fluoride per 100 ml., curve 4 the effect of 10 mg. of phosphorus pentoxide (present as orthophosphate) per 100 ml., and curve 5 the effect of 1 mg. of pyrophosphate per 100 ml. Although nitrite acts as a reducing agent, it also causes a change in hue and the solution becomes yellowish green, probably because of formation of colored products from secondary reactions. Because it forms a reddish complex with ferric ion, thiocyanate causes a change in hue, as shown by a change in the general shape of the curve (Figure 2, curve 2). Iodide not only tends to decrease the intensity of the color because of the removal of ferric ion by reduction, but also to increase the intensity because of the red color of the liberated iodine. Since a number of factors, such as acidity, time, and

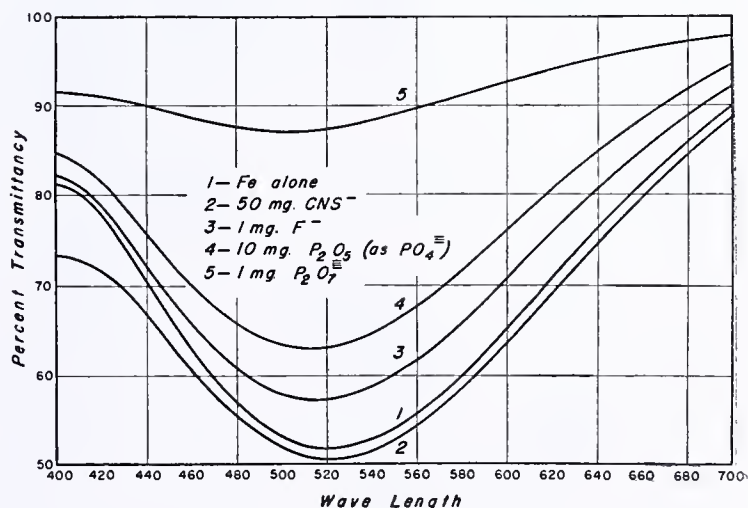


FIGURE 2. EFFECT OF ANIONS

0.5 mg. of iron, diverse ion, and 1 ml. of 10 per cent salicylate in 100 ml. of solution. 1.961-cm. cell



temperature, affect the rate of reduction, it is safest to remove all iodide before making the determination of iron.

The effects of the common anions and their approximate limiting concentrations are listed in Table IV.

TABLE IV. EFFECT OF COMMON ANIONS ON THE COLOR DEVELOPED BY IRON

(0.5 mg. of iron in 100 ml. of solution)				
Ion	Concentration Mg./100 ml.	pH	Apparent Change in Iron Concn. %	Approximate Limiting Concentration Mg./100ml.
Arsenate	50 (As)	2.7	-43.4	...
	10 (As)	2.6	- 2.4	5
Arsenite	50 (As)	2.6	Negligible	...
Borate	150 (B <sub>2</sub> O <sub>3</sub> )	2.5	Negligible	...
Bromide	200	2.6	Negligible	...
Carbonate	200	2.8	Negligible	...
Chlorate	200	2.7	Negligible	...
Chloride	250	2.6	Negligible	...
Citrate	10	2.7	-44.0	0.0
Cyanide	20	2.7	-22.4	...
	2	2.7	- 7.6	0.0
Dichromate	10	2.7	Change in hue	0.0
Fluoride	1	2.7	-15.4	...
	0.3	2.7	- 4.6	0.0
Iodide	100	2.7	-30.0	...
	50	2.6	Variable	0.0
Molybdate	10 (Mo)	2.5	-27.6	...
	3 (Mo)	2.5	- 4.4	...
	1 (Mo)	2.5	Negligible	1.5
Nitrate	200	2.7	Negligible	...
Nitrite	10	2.7	Change in hue	0.0
Orthophosphate	10 (P <sub>2</sub> O <sub>5</sub> )	2.7	-30.2	0.0
Oxalate	10	2.7	-95.4	0.0
Pyrophosphate	1	2.7	-80.0	0.0
Silicate	20 (SiO <sub>2</sub> )	2.6	Slight turbidity	20
Sulfate	250	2.8	Negligible	...
Sulfite	2.5	2.6	- 7.4	0.0
Tartrate	100	2.9	-53.0	...
	50	2.8	-32.2	...
	10	2.7	- 6.0	0.0
Thiocyanate	10	2.7	Change in hue	0.0
Thiosulfate	5	2.7	-11.0	...
	2	2.7	Slowly fades	0.0
Tungstate	10	2.5	-27.2	...
	3	2.5	- 6.8	...
	1	2.5	- 1.6	1.1

Effect of Cations

Interference by cations in colorimetric work is usually regarded as being caused by the color of the ion or by the fact that the ion forms a colored complex with the reagent. In addition, Swank and Mellon (12) have shown that there is very little correlation between the absence of color and the degree of interference, since a cation may form a colorless complex which is more stable than the desired colored complex and in the absence of sufficient reagent a decrease in intensity will result (Figure 3, curve 2). Sagaidachnuii and Ravich (8) state that aluminum forms such a colorless complex with salicylic acid and that an excess of reagent should be used when aluminum is present. As shown above, however, very little

more than the specified 1 ml. of reagent can be added without causing a change in the color. Hence it becomes necessary to limit the amount of aluminum that can be present or else to increase the volume of acetic acid. Examples of colored cations which cause a change in hue are furnished by cupric, cobaltous, nickelous, chromic, and uranyl ions (Figure 2, curves 3 and 4). Manganous ion causes only a slight change in hue. In determining iron in copper alloys Gregory (3) removes the blue color of copper with potassium cyanide.

TABLE V. EFFECT OF COMMON CATIONS ON THE COLOR DEVELOPED BY IRON

(0.5 mg. of iron in 100 ml. of solution)				
Ion	Concentration Mg./100 ml.	pH	Apparent Change in Iron Concn. %	Approximate Limiting Concentration Mg./100 ml.
Aluminum	50	3.0	-26.2	...
	10	2.7	- 3.0	7
Ammonium	250	2.6	Negligible	...
Antimonous	10	...	Precipitates	...
	2	2.6	Negligible	5
Barium	50	2.7	+ 3.4	...
	5	2.6	+ 1.2	15
Beryllium	50	3.1	-10.0	...
	25	2.9	- 1.8	25
Bismuth	10	...	Turbidity	...
	2	2.6	+ 2.0	2
Cadmium	200	2.4	Negligible	...
Calcium	50	2.6	Negligible	...
Chromic	2.5	2.7	Change in hue	0.0
Cobaltous	50	2.6	Change in hue	...
	5	2.6	+ 3.0	3
Cupric	5	2.7	Change in hue	...
	1	2.6	Negligible	1
Lead	100	3.0	Negligible	...
Lithium	150	2.6	Negligible	...
Magnesium	100	2.6	Negligible	...
Manganous	50	2.6	Slight change in hue	25
Mercuric	10	...	Precipitates	0.0
Mercurous	2	...	Slight turbidity	0.0
Nickelous	10	2.6	Change in hue	...
	2	2.6	Negligible	2
Potassium	250	2.6	Negligible	...
Silver	50	...	Precipitates	...
	30	2.7	Negligible	30
Sodium	260	2.6	Negligible	...
Stannic	10	...	Precipitates	0.0
Stannous	10	2.7	Turbidity	...
	5	2.7	Slow fading	0.0
Strontium	50	2.6	Negligible	...
Thorium	50	2.6	+ 7.8	...
	10	2.6	Negligible	20
Uranyl	25 (U)	2.6	Change in hue	...
	10 (U)	2.6	Change in hue	5
Zinc	50	2.7	Negligible	...
Zirconium	1	...	Precipitates	0.0

Great care should be taken, however, in adding potassium cyanide, because, as shown above, a very slight excess of cyanide ion appreciably decreases the intensity of the color of the iron complex. A number of cations interfere because they precipitate or cause a slight turbidity under the conditions of the color formation. In Table V are listed the effect and the approximate limiting concentration for each of the common cations.

Summary

A spectrophotometric study shows that the salicylic acid method for the determination of iron colorimetrically is satisfactory, provided experimental conditions are carefully controlled.

The optimum pH value is 2.6 to 2.8. Not more than 1 ml. of reagent and 12 ml. of 1 to 1 acetic acid should be used.

The color system follows Beer's law.

The color is stable in diffuse light for 66 hours. All solutions should be protected from direct sunlight, however.

The extent of the interference of a considerable number of the common ions is great enough to require their removal before the determination is made.

Acknowledgments

The writer wishes to express his sincere appreciation to M. G. Mellon of Purdue University, in whose laboratory this in-

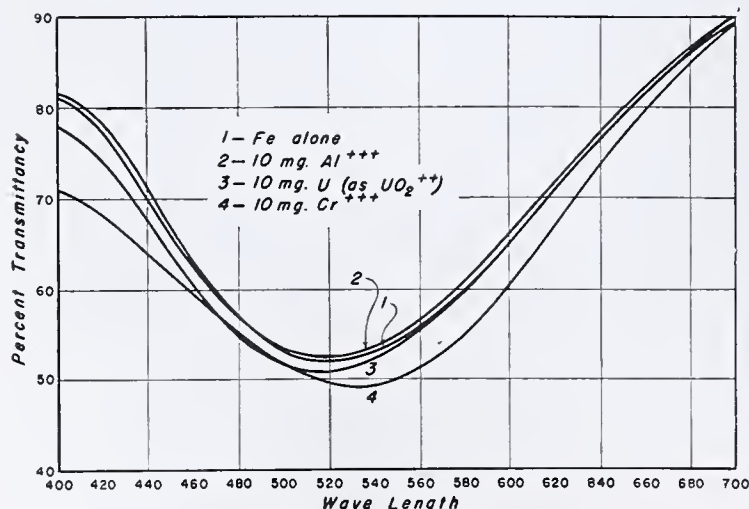


FIGURE 3. EFFECT OF CATIONS

0.5 mg. of iron, diverse ion, and 1 ml. of 10 per cent salicylate in 100 ml. of solution. 1.961-cm. cell



Investigation was carried on, for his interest and helpful suggestions and to thank him for the privilege of using the Purdue spectrophotometer. Thanks are also given to W. B. Fortune of Purdue for his profitable criticism and for preparing standard solutions of ions and adjusting the spectrophotometer.

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# Platinized Silica Gel as a Catalyst for Gas Analysis

## Complete Oxidation of Methane and Ethane

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IT HAS been shown (2) that hydrogen can be quantitatively oxidized by adding oxygen to the hydrogen-hydrocarbon residue remaining after carbon monoxide absorption and passing the gas over platinized silica at 100° C. The copper oxide tube was replaced by a catalyst tube similar in design, containing 1 gram of a commercial platinized silica gel. Complete oxidation of carbon monoxide did not occur at temperatures below 300° C. At this temperature (3) oxidation of ethane and higher hydrocarbons occurred to a slight extent; so the absorption method for carbon monoxide was recommended when the catalyst-tube method was used in the presence of higher hydrocarbons.

TABLE I. OXIDATION OF METHANE AND ETHANE

Analysis	Methane						Ethane	
	1	2	3	4	5	6	7	8
Temp., ° C.	655	610	610	565	610	610	620	615
No. of passes	4	4	4	15	4	3	3	3
Rate, ml. per minute	50	50	75	50	75	75	65	65
% in analyzed mixture, %	30	30	30	30	50	65	30 to 35	
H <sub>2</sub> by explosion, %	12.5	12.5	12.5	12.5	8.8	6.2	C <sub>2</sub> H <sub>6</sub>	6.5
H <sub>2</sub> by catalyst, %	12.5	12.4	12.4	11.8	8.7	6.2	C <sub>2</sub> H <sub>6</sub>	6.5

The latter study (3) was to determine the lowest temperature at which any oxidation of the hydrocarbon occurred; no work was done to determine whether the oxidation of the hydrocarbons could be made complete. If oxidation of the methane hydrocarbons could be made complete at some temperature, the catalyst-tube method could be used for both hydrogen and hydrocarbons by simply raising the temperature after hydrogen oxidation. The results of such a study are reported in this paper.

### Apparatus and Gases

The apparatus was that used in the previous work, except that the copper oxide tube was replaced by a similar Pyrex tube containing 1 gram of the commercial platinized silica gel containing 0.75 per cent of platinum produced by the Silica Gel Corporation. The limiting temperature of the standard heater is 400° C., at which temperature methane is only partially oxidized. The heating element was removed from the steel shell and replaced

by a heating element for a coal volatile-matter furnace. This gave a heating chamber 15 × 3.75 cm. (6 × 1.5 inches) and could attain a temperature of 950° C. The heater was connected in series with a variable-plate resistance by which the temperature could be controlled. Temperature was measured with a mercurial thermometer (Palo-Myers No. 8006F., range 280° to 650° C. in 1° C.) which was placed within the heater in the usual manner for the hydrogen determination. The methane and ethane were obtained in cylinders from the Ohio Chemical Company.

### Oxidation of Methane and Ethane

The previous work showed that the oxidation of ethane and higher hydrocarbons began at temperatures considerably below that for methane. If complete methane oxidation can be secured, it may be concluded that oxidation of the higher hydrocarbons will also be complete.

A stock mixture of methane or ethane, oxygen, and nitrogen was made and samples of this gas were diluted with oxygen to give a volume of approximately 100 ml. for analysis. Methane was determined by the explosion and catalyst-tube methods for each sample. The gas was passed from the buret through the catalyst tube to the explosion pipet and back to the buret again through the catalyst. This double passage through the catalyst is called a pass in Tables I and II.

TABLE II. OXIDATION OF HYDROGEN AND METHANE

Analysis	1	2	3	4
Temperature, ° C.	610	610	620	620
Number of passes	6	2	3	3
Rate, ml. per minute	50	15	15	25
CH <sub>4</sub> , %				
By explosion	13.0	6.3	5.8	5.8
By catalyst	13.1	6.5	5.9	5.9
H <sub>2</sub> , %				
By explosion	21.7	11.9	9.9	9.9
By catalyst	21.6	11.5	10.1	9.7

The minimum temperature for the complete oxidation of methane was determined and the effect of excess oxygen studied. The results are given in Table I.

A temperature of 610° C. is necessary, for analysis 4 at 565° C. shows incomplete oxidation after 15 passes through the catalyst. As long as a small excess of oxygen remains,



complete oxidation is obtained. However, larger percentages of excess oxygen permit faster passage of the gas through the catalyst tube.

### Oxidation of Hydrogen and Methane

Mixtures of hydrogen, methane, oxygen, and nitrogen were made and analyzed by both explosion and catalyst-tube methods for comparison. In the catalyst-tube method hydrogen and hydrocarbons were oxidized together at 610° C. and from the volume decrease and carbon dioxide the hydrogen and methane were calculated. The results are given in Table II. If hydrogen is to be determined separately, the catalyst tube is held at 100° C. and the hydrogen is oxidized; the temperature is then increased to 610° C. and the hydrocarbons are oxidized and calculated to methane and ethane.

### Discussion

Methane and ethane are completely oxidized over commercial platinized silica gel at 610° C. It may be assumed that higher hydrocarbons are also completely oxidized, as previous work (3) shows that they are more readily oxidized than meth-

ane. The recommended procedure is to absorb all possible components of the gas mixture, including carbon monoxide, and determine hydrogen and hydrocarbons over the catalyst at 610° C. As carbon monoxide is oxidized at 300° C., carbon monoxide, hydrogen, and methane may be determined by oxidation at 620° C. (1). Hydrogen may be determined by oxidation at 100° C. and the temperature of the catalyst tube raised to 610° C. for the hydrocarbon determination.

### Conclusions

Methane and ethane are completely oxidized by excess oxygen over a platinized silica gel catalyst at 610° C. The catalyst-tube method may be used for the determination of hydrogen and hydrocarbons, either singly or together, by the use of the proper oxidation temperature.

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# Determination of Unsaturation in Organic Compounds

## By Means of the Mercury-Catalyzed Reaction with Standard Bromate-Bromide

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IT HAS been known for a long time that the reaction of bromine with compounds having a triple bond does not go to completion rapidly. In the case of acetylene, Davis, Crandall, and Higbie (2) showed that the slowness and incompleteness of the reaction is due to the presence of oxygen, and that the reaction is aided by aluminum, mercury, and nickel salts. Mulliken and Wakeman (8) found that in general liquid alkynes and alkadienes do not react quantitatively with standard bromate-bromide solution. Recently (4) the analysis of acetylene in aqueous solution has been carried out quantitatively in the presence of mercuric sulfate, and without taking precautions against oxygen. In the attempt to develop a method for determining unsaturation, a study has been made of the behavior of bromate-bromide solution, in the presence and in the absence of mercuric sulfate, with a number of unsaturated compounds, some having a triple and some a double bond.

### Materials

C. P. glacial acetic acid was used in addition to the reagents previously described (4). Carbon tetrachloride was purified by saturating with chlorine, exposing to direct sunlight for 10 to 12 hours, washing with aqueous sodium hydroxide, and drying with calcium chloride. It distilled at 75.6° C. uncorrected. Several unsaturated compounds were prepared for this work. The following were used after purification: dichloroethylene (Eastman's), distilled once; maleic acid (Pfanstiehl); fumaric acid (Eastman's); and cinnamic acid, crystallized twice.

### Preparation of Solutions for Analysis

Aqueous solutions of water-soluble compounds were made by weighing sufficient material directly into a volumetric flask so that, when made to volume, the liquid was approximately 0.08 *N* in unsaturation and the sample taken, 25 ml.,

had about two milliequivalents of unsaturation. Hydrocarbons and water-insoluble compounds were dissolved in carbon tetrachloride as follows:

A sealed ampoule of the substance, having approximately 60 milliequivalents of unsaturation, is placed in a weighed, glass-stoppered bottle of 150-ml. capacity and rather wide mouth. Some carbon tetrachloride is added, the ampoule is broken, and the bottle is filled with the solvent so that there is only a small air space, tightly stoppered, weighed, and shaken. From the weights of the two liquids, the density of the carbon tetrachloride at the temperature of pipetting and the approximate density of the solute, a volume of the solution, and likewise a concentration of the solute can be calculated, assuming additivity of volumes (perfect solution).

By fitting the bottle with a two-hole rubber stopper carrying a separatory funnel (stem reaching to the bottom) and a tube through which a pipet can be inserted, a sample can be forced into the pipet by allowing mercury to flow from the separatory funnel. There should be a small air space between the liquid and the stopper to prevent direct contact, but it should be small, to minimize errors due to difference in volatility of solvent and solute. The pipet, with a three-way stopcock, is calibrated to contain a definite volume (3). The stopcock is lubricated with a water-soluble grease. With a pipet holding 5.6 ml., and with the solution about 0.42 *N* in unsaturation, the sample delivered has about two milliequivalents of unsaturation. This procedure permits the removal of successive portions of the solution without any change in concentration.

### Analytical Procedure

The analytical procedure is based upon that described by Frieman, Kennedy, and Lucas (4).

A calculated excess (10 to 15 per cent) of 0.1 *N* bromate-bromide solution (about 25 ml.) is run from a buret into a 300-ml. conical flask having a ground-glass stopper bearing a sealed-in stopcock. (The first analysis of the solution is approximate only, and should be carried out with a larger excess of bromate-bro-



mide solution. From this preliminary result the desired excess can be calculated.)

Following the evacuation of the flask by means of a water aspirator, 5 ml. of 6 *N* sulfuric acid are added and the flask is allowed to stand 2 to 3 minutes while bromine is being liberated. Next, 10 to 20 ml. of 0.2 *N* mercuric sulfate and the solution to be analyzed, which should have about two milliequivalents of unsaturation, are run in. The volume of the carbon tetrachloride wash liquid should be about 15 ml. Following this, 20 ml. of glacial acetic acid are added. In the case of water-soluble substances, the acetic acid is omitted. After the flask, wrapped in a black cloth, has been shaken for about 7 minutes, 15 ml. of 2 *N* sodium chloride and 15 ml. of 20 per cent potassium iodide are added in succession, and the shaking is continued for 0.5 minute. The vacuum is broken and the titration made with 0.05 *N* sodium thiosulfate, using starch. A blank, without the sample and with one-third of the amount of bromate-bromide solution used in the analysis, is run at the same time, and under the same conditions.

The excess of bromate-bromide should not exceed 10 to 15 per cent; otherwise errors due to substitution may become appreciable. If the excess is less, the rate of addition may become so slow towards the last that the reaction is not quantitative in the time specified. The molar ratio of mercuric ion to final bromide ion should be greater than unity, otherwise the mercuric salt has insufficient catalytic effect. The presence of acetic acid greatly aids the reaction when carbon tetrachloride is present, no doubt because of the increased solubility of the unsaturated compound in the aqueous phase. The results are more reproducible in its presence, since the decrease in the time of bromination cuts down the amount of substitution. Sodium chloride is necessary, in order to liberate free bromine from its complex with mercuric sulfate. The iodine-starch end point, rather than the iodine-carbon tetrachloride end point, is used, because, in the presence of acetic acid, the solubility in the aqueous phase is so enhanced that the iodine imparts but a faint pink color to the carbon tetrachloride while the aqueous phase is a deep yellow. Actually, this solubility relationship is an aid in the titration. The blank is run with only one-third, instead of the entire amount of bromate-bromide solution, in order better to approximate an average of the bromine concentration during an analysis. The correction is usually about 0.5 per cent.

**CHANGES OBSERVED DURING ANALYSES.** The deep orange bromine color, which develops when sulfuric acid is added to the bromate-bromide solution, bleaches slightly as the mercuric sulfate is run in. Sometimes a precipitate, presumably mercuric bromide, forms at the same time. Addition of the sample causes a further bleaching, so that apparently little or no free bromine is present. The color deepens upon the addition of the sodium chloride. If one changes the order of addition in the case of the water-soluble compounds, propiolic, maleic, fumaric, and cinnamic acids, in the absence of both carbon tetrachloride and acetic acid, a sudden and complete bleaching occurs as soon as the molar ratio of mercuric ion to bromide ion reaches unity. This effect is explainable on the assumption that excess mercury is needed before the reaction is catalyzed appreciably.

Under certain conditions, bromination of purely aliphatic alkynes is aided by the formation of a thick, viscous emulsion. The conditions are absence of acetic acid, a mercury-bromide ratio close to unity, and a bromate excess of about 5 per cent.

**VARIATIONS IN PROCEDURE.** The importance of mercuric sulfate in the bromination is shown by comparing No. 3 with No. 1 and No. 2, Table I, and also by comparing the results in Table II, with and without mercury. From No. 1, Table I, it is evident that a large excess of mercury has no advantage over a small excess. In general, the bromination of alkynes and alkenes proceeds quantitatively when the mercury-bromide ratio is greater than unity, and that of the alkynes is very unsatisfactory in the absence of mercury. In addition to the alkynes, the bromination of some other unsaturated compounds, which is unsatisfactory in the absence of mercury, is

TABLE I. EFFECT OF VARIATIONS IN ANALYTICAL PROCEDURE

(Volume of CCl <sub>4</sub> = 20 ml.)						
Compound	HgSO <sub>4</sub> /Br <sup>-</sup> Ratio	HOAc	KBrO <sub>3</sub>	Time	Error	
		Ml.	%	Min.	%	
Mercury-Bromine Ratio						
1	2-Heptyne	2.4	20	7	- 3.2 <sup>a</sup>	
2	2-Heptyne	1.2	20	7	- 4.1 <sup>a</sup>	
3	2-Heptyne	0.0	20	7	-23.0 <sup>a</sup>	
Acetic Acid						
4	Phenylacetylene	1.1	25	7	- 3.0	
5	Phenylacetylene	1.1	0	7	-23.0	
6	1-Hexyne	1.1	25	5	- 0.9	
7	1-Hexyne	1.1	0	5	-10.0	
Excess Bromate						
8	1-Pentyne	1.0	0	25	+12.0	
9	1-Pentyne	1.7	0	12	+ 7.5	
10	1-Pentyne	1.7	0	5	+ 5.5	
Time of Bromination						
11	1-Heptyne	1.5	15	15	60	- 2.1
12	1-Heptyne	1.5	15	15	30	+ 2.7
13	1-Heptyne	1.5	15	15	15	+ 2.7
14	Phenylacetylene	1.1	20	10	30	+ 3.7
15	Phenylacetylene	1.1	20	10	5	0.0
Condition of Sample: Sunlight						
16	2-Heptyne	1.2	20	15	7	- 3.2 <sup>a</sup>
17	2-Heptyne	1.2	20	15	7	- 0.2 <sup>b</sup>
Condition of Sample: Aging						
18	1-Heptyne	1.2	15	25	15	-17.5 <sup>c</sup>
19	1-Heptyne	1.5	15	15	15	+ 2.7 <sup>d</sup>

<sup>a</sup> CCl<sub>4</sub> solution was exposed to direct sunlight for 1 hour.

<sup>b</sup> Before exposure of same solution to sunlight.

<sup>c</sup> Sample of hydrocarbon was 5 weeks old.

<sup>d</sup> Hydrocarbon redistilled.

made quantitative in its presence—viz., dichloroethylene, maleic acid, and fumaric acid. On the other hand, cinnamic acid, which reacts satisfactorily in the absence of mercury, undergoes substitution when mercury is present. Dimethylbutadiene gives low results and propiolic acid gives very low results in the absence of mercury, while in its presence both give high results, the latter much the worse. In more concentrated solutions, however, it has been found in this laboratory by Saul Winstein that dimethylbutadiene in carbon tetrachloride solution and in the absence of mercury gives fairly good results, but still low by 2 to 3 per cent.

The effect of acetic acid is shown in Table I by comparing No. 4 with No. 5, and No. 6 with No. 7. In general, the reaction proceeds more rapidly and with greater reproducibility of results when acetic acid is present. An interesting case is that of dichloroethylene, which reacts rapidly in the presence of mercury when acetic acid is present and slowly when carbon tetrachloride is present, but scarcely reacts at all in the absence of mercury and carbon tetrachloride.

The effect of excess bromate is shown by Nos. 8, 9, and 10, Table I. These were among the first experiments. Since an excess was shown to be undesirable, subsequent runs were carried out with only small excess. The effect of a large excess in the presence of acetic acid was not tested.

Variation in the time, with the exception of dimethylbutadiene and propiolic and cinnamic acids, has little effect upon the results, provided the addition reaction is completed. In general, 7 minutes are sufficient, when the general procedure is followed. However, the reaction with maleic and fumaric acids in water and in presence of mercury is so slow that a half hour should be allowed. Cinnamic acid dibromide is appreciably substituted in the presence of mercury. Freshly precipitated cinnamic acid reacts quantitatively with 1 mole of bromine in 3 minutes (Table II), but with no more, even after 35 minutes. But when mercuric sulfate is added at the end of 4 minutes, an additional 1/3 mole reacts within 1 minute. Increased substitution, with time, in the presence of mercury, takes place also with dimethylbutadiene and with propiolic acid. In the latter case the limit is one additional mole of bromine.



TABLE II. BROMINATION WITH AND WITHOUT MERCURIC SULFATE

Substance	HgSO <sub>4</sub> / Br <sup>-</sup> Ratio	HOAc	CCl <sub>4</sub>	Time Min.	Taken Milliequivalents	Found	Error %	Substance	HgSO <sub>4</sub> / Br <sup>-</sup> Ratio	HOAc	CCl <sub>4</sub>	Time Min.	Taken Milliequivalents	Found	Error %
		ML.	ML.							ML.	ML.				
Mercuric Sulfate Present								Mercuric Sulfate Absent							
1-Pentyne	1.3	0	20	2	1.83	1.89	+ 2.2 <sup>a</sup>	1-Hexyne	...	0	20	30	1.685	0.99	-41
1-Hexyne	1.1	0	20	3	1.685	1.70	+ 0.9 <sup>b</sup>	1-Hexyne	...	20	20	10	2.26	1.26	-44
1-Heptyne	1.2	0	20	35	2.22	2.25	+ 1.3 <sup>c</sup>	1-Heptyne	...	0	20	30	2.21	1.34	-39
1-Heptyne	1.5	15	20	7	1.78	1.76	- 1.6 <sup>d</sup>	1-Heptyne	...	15	20	5	1.78	0.94	-50
2-Heptyne	1.2	0	20	10	2.05	1.97	- 4.0 <sup>e</sup>	2-Heptyne	...	0	20	10	1.84	1.35	-26
2-Heptyne	1.2	20	20	7	2.15	2.08	- 3.5	2-Heptyne	...	20	20	7	2.05	1.60	-23
Phenyl acetylene	1.1	25	20	7	3.03	3.02	- 0.3	Phenyl acetylene	...	20	20	7	3.03	2.71	-11
Propiolic acid	1.3	0	0	2	2.21 <sup>f</sup>	3.26	+56	Propiolic acid	...	0	0	15	2.21 <sup>f</sup>	0.38	-78
Cyclohexene	1.2	15	20	3	2.275	2.285	+ 0.4 <sup>g</sup>	Cyclohexene	...	0	20	3	2.275	2.27	- 0.2
1-Hexene	1.3	15	20	3	2.95	2.98	+ 1.0	1-Hexene	...	0	20	5	2.95	2.95	0.0
2,3-Dimethyl- butadiene	1.1	15	20	5	1.60	1.97	+20	1-Hexene	...	15	20	3	2.95	2.94	- 0.3
Dichloroethylene	1.4	0	20	70	1.73	1.72	- 0.5	2,3-Dimethyl- butadiene	...	0	20	5	1.60	1.13	-29
	1.2	20	0	5	1.97	1.97	0.0	2,3-Dimethyl- butadiene	...	15	20	5	1.60	1.04	-35
Mixture of phenyl acetylene and cyclohexene	1.3	15	20	5	1.93	1.96	+ 1.6	Dichloroethylene	...	0	0	100	1.73	1.12	-30
Maleic acid	1.3	0	0	25	1.79	1.77	- 1.1		...	20	0	20	1.97	0.05	-98
Fumaric acid	1.7	0	0	30	1.401	1.407	+ 0.4	Maleic acid	...	0	0	20	1.79	0.03	-98
Cinnamic acid	1.2	0	0	5	1.35	2.25	+67	Fumaric acid	...	0	0	10	1.40	0.015	-99
								Cinnamic acid <sup>h</sup>	...	0	0	3	1.355	1.40	+ 3.3

<sup>a</sup> Mean of four results, average deviation, 0.5.<sup>b</sup> Mean of two results, average deviation, 0.2.<sup>c</sup> Mean of four results, average deviation, 1.3.<sup>d</sup> Mean of two results, average deviation, 0.5.<sup>e</sup> Mean of three results, average deviation, 1.4.<sup>f</sup> Amount determined by acidimetry.<sup>g</sup> Mean of two results, average deviation, 0.1.<sup>h</sup> As the sodium salt.

The bromine absorbed by a compound having a triple bond may run low if the substance has been exposed to air for some time. Presumably, this is due to absorption of oxygen. The effect is intensified by exposure to sunlight (16 and 17, Table I). Distillation removes the material which is responsible for the low result (18 and 19, Table I).

In Table II are listed some typical results obtained by brominating in the presence and in the absence of mercuric sulfate.

**CONCLUSIONS.** The procedure proposed constitutes a method of determining unsaturation in many unsaturated compounds, and is valuable for alkynes, which react but slowly in the absence of mercuric sulfate. It is important that these alkynes be freshly distilled, and that their solutions in carbon tetrachloride be not exposed to direct sunlight. However, the fact that the mercuric salt catalyzes substitution in some cases, indicates that broad generalizations cannot be drawn. Instead it will be necessary to study each unsaturated compound separately.

### Preparation of Materials

Pentyne-1 was made according to the method of Bourguell (1) by refluxing 2,3-dibromopentane (from 2-pentene and bromine) with xylene and sodamide, the last prepared according to Vaughn, Vogt, and Nieuwland (12); boiling point 38–40° C., uncorrected.

The method of Lebeau and Picon (6, 10) was followed in the preparation of 1-hexyne and 1-heptyne by reacting sodium acetylide with 1-bromobutane and 1-bromopentane, respectively. Alkene present was largely removed along with the ammonia, by allowing the mixture to come to room temperature before decomposing the sodium alkynylide with ice. The temperature was kept low, in order to avoid the isomerizing effect of concentrated sodium hydroxide solution. Two fractionations through a 45-cm. (18-inch) column of glass helices (13) gave 1-hexyne of boiling point 69.7° to 70.1° C., uncorrected, yield 30 per cent. The 1-heptyne was fractionated twice as above, boiling point 98° to 100° C., uncorrected, yield 37 per cent, and later, in order to remove oxygen absorbed on standing, through a Vigreux column in an atmosphere of nitrogen; boiling point 97.5° to 97.9° C., uncorrected.

For the preparation of 2-heptyne, sodium hexynylide was reacted with methyl sulfate following the general procedure of Meinert and Hurd (7). However, methyl sulfate is less satisfactory than the iodide, probably because it reacts more rapidly with ammonia. The inferiority of sulfates to bromides and iodides has been shown by Vaughn, Hennion, Vogt, and Nieuwland (11). After drying and fractionating twice through the column, the product, in 10 per cent yield, boiled at 109.3–109.9° C. Vaughn et al. (11) give 107–111° C.

Phenylacetylene was synthesized by the method of Hessler (5). It was distilled through a Vigreux column in an atmosphere of nitrogen. The fraction distilling at 139.8–140.6° C. was used.

Propiolic acid was prepared from succinic acid through dibromosuccinic acid (9). The pure compound was not obtained; the distillate containing some water, coming over at 40° to 83° C. under 130 mm., was used without further purification. The propiolic acid was determined by titration against standard alkali. It was assumed that no other organic acid was present. Cyclohexene, 1-hexene, and 2,3-dimethylbutadiene were kindly supplied by Saul Winstein, of this laboratory. Their boiling points were, respectively, 82.6–82.7°, 63.2–63.7°, and 68.3–68.4° C., corrected. The first two were distilled from sodium before use.

### Summary

In the presence of mercuric sulfate several alkynes and alkenes were found to react quantitatively with bromine, two moles and one mole, respectively. These are 1-pentyne, 1-hexyne, 1-heptyne, 2-heptyne, phenylacetylene, 1-hexene, cyclohexene, and dichloroethylene. A general analytical procedure which is applicable to such compounds is described. In some cases, however, the reaction, although quantitative, may be slow—for example, maleic and fumaric acids. In other cases substitution as well as addition may take place—for example, propiolic acid, 2, 3-dimethylbutadiene, and cinnamic acid. In the case of alkynes, the analysis should be carried out on freshly made solutions of recently distilled products, in order to avoid the errors due to absorbed oxygen.

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# Direct Determination of Available P<sub>2</sub>O<sub>5</sub> Content of Fertilizers

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THE "official" method (1) for "available" P<sub>2</sub>O<sub>5</sub> content of commercial fertilizers was based upon the procedure of Fresenius, Neubauer, and Luck (6) for determining the phosphatic components other than undecomposed rock residues. Adopted by the Association of Official Agricultural Chemists in 1884 (2), the method has been a most dependable procedure for the evaluation of phosphatic fertilizers of acidic character. It was proposed and intended, however, solely for products characterized by free acid, monocalcium, iron, and aluminum phosphates.

In recent years, ammoniation and incorporation of either dolomite or rock phosphate supplements have become common practices in the fertilizer industry. These practices have developed types of fertilizers (4, 24) that contain considerable quantities of dibasic phosphates (9, 10, 21, 22) and variable amounts of tricalcium compounds that develop during processing and curing (11, 13, 15, 23). Moreover, engendered tricalcium phosphate and component fluorides react to form fluorapatite during both curing and analysis by the official method (17, 20).

Seven years ago, the associate referee listed the objective, to find a laboratory method that will be applicable to the valuation of ammoniated, as well as straight superphosphates," and recommended "that a further study be made of the method for citrate-insoluble phosphoric acid with a view to modification that will secure more concordant results" (32). The subsequent decrease of analytical charge to 1 gram was admittedly an advance, but the inherent difficulties were not overcome by that change.

The official procedure for available P<sub>2</sub>O<sub>5</sub> calls for two eliminative manipulations and two P<sub>2</sub>O<sub>5</sub> determinations for each analysis. Obviously, it would be advantageous to have a rapid and dependable technic for direct determination of available P<sub>2</sub>O<sub>5</sub> content by means of a solvent capable of effecting the same removals now made by aqueous leaching and citrate digestion.

## Objectives and Principle of Proposed Procedure

The objective of the present study was the development of a simple, rapid, and economical direct analytical procedure for all types of phosphatic fertilizers. Choice of solvent was restricted to one exerting practically the same capacity as the official citrate solution for undecomposed rock and conducive to complete precipitation of its P<sub>2</sub>O<sub>5</sub> content. The studies led to a procedure that prescribes a single solvent for prior leaching and subsequent steam digestion of leached residue, combination of leachate and digestate to volume, and one P<sub>2</sub>O<sub>5</sub> determination.

Direct solvent action alone enters into the dissolving of acidic phosphates, but the analysis of basic products involves exchange between the NH<sub>4</sub> of a boiling citrated *M* solution of ammonium nitrate and the bases of the phosphatic compounds not removed by prior leaching. The engendered ammonia is removed almost instantaneously by a balanced passage of steam which maintains near-constancy of pH and volume during digestion. Use of a steam current also expedites the dissolving of the phosphates, affords vigorous agitation, assures uniform suspension of the solids, eliminates lumping, and requires a minimum of attention. Direct boil-

ing and water replacements were found to be much less expeditious than a current of steam in effecting removals of engendered ammonia.

The importance of rapid elimination of ammonia engendered in the boiling digestions of *M* ammonium nitrate is shown by the preliminary trials of Table I. The mean of the P<sub>2</sub>O<sub>5</sub> extractions from the six systems purged of ammonia by current of steam was 2.2 times the corresponding mean of the P<sub>2</sub>O<sub>5</sub> extractions from the refluxed digestions. Higher final pH value and lower solvent capacity for refluxed digestions are shown for each of the six digestions of basic phosphates. Since the initial volume of the *M* nitrate solution was maintained in both of the boiling techniques, pH constancy and greater solvent action are attributable to expeditious removal of engendered ammonia and effective dispersion of the solids by the vigorous current of steam.

The reactions that take place between the basic phosphates and ammonium nitrate during the steam digestion may be assumed to produce a solution of monoammonium phosphate, as indicated by the equations



## Scope of Present Studies

Some of the extensive pilot studies that preceded adoption of the ultimate solvent and technic will be given subsequent to the presentation of the proposed procedure and analytical comparisons. For brevity, the term "solvent" will be used to connote an *M* ammonium nitrate-0.05 *M* ammonium citrate solution of 4.2 pH. The capacities of official citrate solution and proposed solvent were compared for samples of widely variant type, origin, and concentration, in a study of the several factors—composition, size of charge, particle size, common ion effect, concentration and constancy of pH of solvent, period of digestion, raw rock supplements, P<sub>2</sub>O<sub>5</sub> transitions induced during analysis, and variable proportions of the basic forms of phosphates engendered during commercial processing and aging.

TABLE I. COMPARATIVE SOLVENT ACTION EXERTED BY *M* AMMONIUM NITRATE<sup>a</sup>

(Sustained volume, 100 ml., during boiling with and without passage of steam, in evaluation of P<sub>2</sub>O<sub>5</sub> content of basic phosphatic materials)

Phosphatic Material Type	Charge Gram	Boiling and Using Reflux Condenser		Boiling with Injection of Current of Steam	
		Final pH of extract	P <sub>2</sub> O <sub>5</sub> dissolved Mg.	Final pH of extract	P <sub>2</sub> O <sub>5</sub> dissolved Mg.
c. p. dicalcium phosphate	0.25	6.0	68	4.0	129
c. p. tricalcium phosphate	0.25	6.0	27	4.2	101
Calcined rock phosphate	0.25	6.6	36	4.4	88
Fused rock phosphate	0.25	6.2	48	4.0	73
Ammoniated superphosphate	0.50	5.0	26	4.0	42
Limed superphosphate	0.50	5.6	6	4.0	37

<sup>a</sup> Contained no citrate.



## Direct Determination of $P_2O_5$ -Availability in Fertilizers by Citrated Ammonium Nitrate

**CITRATED AMMONIUM NITRATE SOLVENT.** Prepare a stock solution, each liter to contain 80 grams of  $P_2O_5$ -free ammonium nitrate, 50 ml. of  $M$  citric acid, and 75 ml. of  $M$  ammonium hydroxide. This dual salt solution ( $M$  nitrate-0.05  $M$  citrate) should have a pH of 4.2.

**PROCEDURE FOR MIXED FERTILIZERS.** Weigh a 1.0-gram charge into a small porcelain dish; wet carefully with 5 ml. of solvent, triturate, transfer onto a 9-cm. gravity filter, and leach into a 150-ml. beaker with several 10-ml. portions of the cold solvent. Add 0.5 ml. of 0.04 per cent solution of bromocresol green to the leachate. If a blue or bluish green color develops, add dropwise sufficient 1 + 9 nitric acid to produce a change to light green. Continue leaching to a final volume of 100 ml., and maintain color as before. Transfer the filter to the 250-ml. "fertilizer" flask, *A* of Figure 3, and add 100 ml. of the solvent. Stopper the flask tightly and disintegrate the filter by vigorous agitation. Rinse the stopper and the neck of the flask with a small amount of distilled water. Adjust outlet *B* to trap *E* and bring the suspension to boiling by means of a small Bunsen burner, *C*, provided with a flame guard. Connect tube *D* with a steam generator and pass steam through the suspension in flask *A* for 30 minutes, regulating flame to maintain volume of approximately 100 ml. Remove flame and disconnect flask from steam generator; wash both outside and inside of inlet tube and the liquid from the safety tube, back into the digestion flask, *A*. Place an inverted beaker over the neck of the flask and cool under tap and then add the prior 100-ml. leachate; make to volume and mix. Filter a sufficient quantity through an 18.5-cm. fluted filter, and discard the first 25 to 40 ml. Use a 25-ml. (0.1-gram equivalent) aliquot and precipitate ammonium phosphomolybdate as in the official method.

**PROCEDURE FOR STANDARD SUPERPHOSPHATES.** Proceed as for mixed fertilizers, but reduce the steam digestion period to 15 minutes.

**PROCEDURE FOR TRIPLE SUPERPHOSPHATES.** Proceed as for standard superphosphates, but use a 0.5-gram charge.

**PROCEDURE FOR CALCINED AND FUSED ROCK PHOSPHATES.** Use a 0.5-gram charge and proceed as for mixed fertilizers.

**PROCEDURE FOR BONE MEAL.** Proceed as for mixed fertilizers.

**PROCEDURE FOR BASIC SLAG.** Proceed as for mixed fertilizers.

**PROCEDURE FOR METAPHOSPHATES.** Proceed as for calcined and fused rock phosphates. Hydrolyze a 10-ml. aliquot by

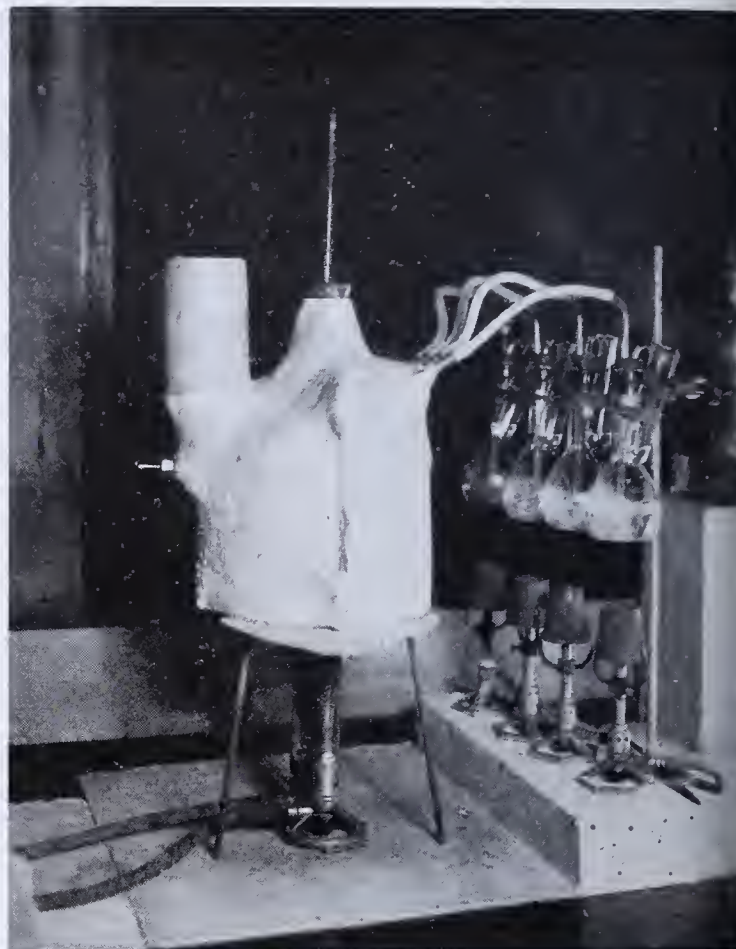


FIGURE 2. STEAM GENERATOR OF FIGURE 1, AFTER INSULATION AND CONNECTION WITH DIGESTION FLASKS AND GUARDS

digestion with 5 ml. of concentrated nitric acid at the boiling point for 15 minutes, cool, nearly neutralize, and proceed as in the official method.

**PROCEDURE FOR ROCK PHOSPHATES.** Introduce directly into flask *A*, 1-gram charge and 100 ml. of solvent, and proceed to digest as in mixed fertilizers. Cool and make to volume. Filter, and refilter if necessary, until filtrate is perfectly clear. Use a 25-ml. aliquot and proceed as in the official method.

## Experimental

**INCLUSION OF CITRATE IN SOLVENT.** Following preliminary trials,  $M$  concentration of ammonium nitrate was used in all comparisons. Boiling steamed digestions with this solution gave values comparable with those obtained by the official methods for some materials, but not for all. Pilot studies were then conducted as to the effect induced by the inclusion of 0.025  $M$  and 0.05  $M$  concentrations of ammonium citrate in the  $M$  ammonium nitrate solution. Both concentrations enhanced the capacity of ammonium nitrate solution to dissolve superphosphates of high iron content, ammoniated superphosphates, basic slags, and bone meals. The 0.05  $M$  citrate concentration imparted maximal capacity to the  $M$  ammonium nitrate solution in comparison with the official procedure and was therefore adopted for the prescribed solvent.

Results by the official method and by steam digestions of ammonium nitrate, alone and with inclusion of 0.05  $M$  ammonium citrate, are given in Table II. In the absence of the citrate, values by ammonium nitrate digestions were invariably less than by the official method. Comparable values were obtained, however, for the acidic materials by citrate and solvent digestions. A somewhat higher value was found for the ammoniated triple superphosphate by solvent. The value for the precipitated tricalcium phosphate by the conventional citrate digestion was only 42.6 per cent as against 97 per cent by digestion with solvent.

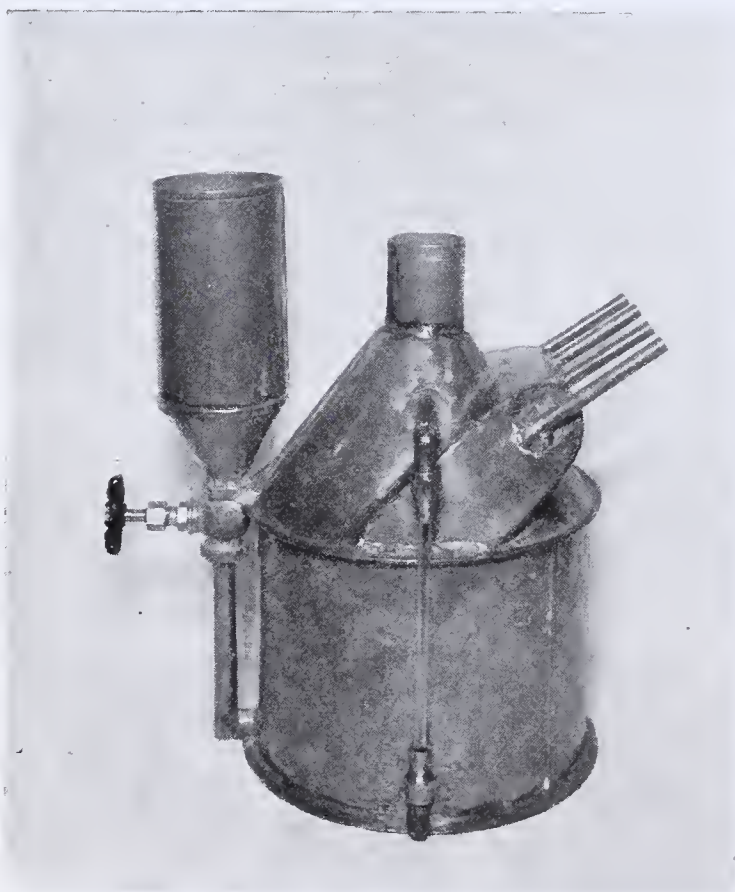


FIGURE 1. HOME-MADE COPPER 4-UNIT STEAM GENERATOR



Quantitative precipitation of ammonium phosphomolybdate cannot be made from the official citrate solution, even after dilution of one-tenth aliquots. Direct  $P_2O_5$  precipitations from solvent can be made quantitatively, however, since its citrate concentration is only one-ninth of that of the official solution. With aliquots of solvent containing 2.25, 4.5, 9.0, and 18 mg. of  $P_2O_5$ , no retardation of molybdate precipitation was indicated until citrate content was five times that stipulated for solvent.

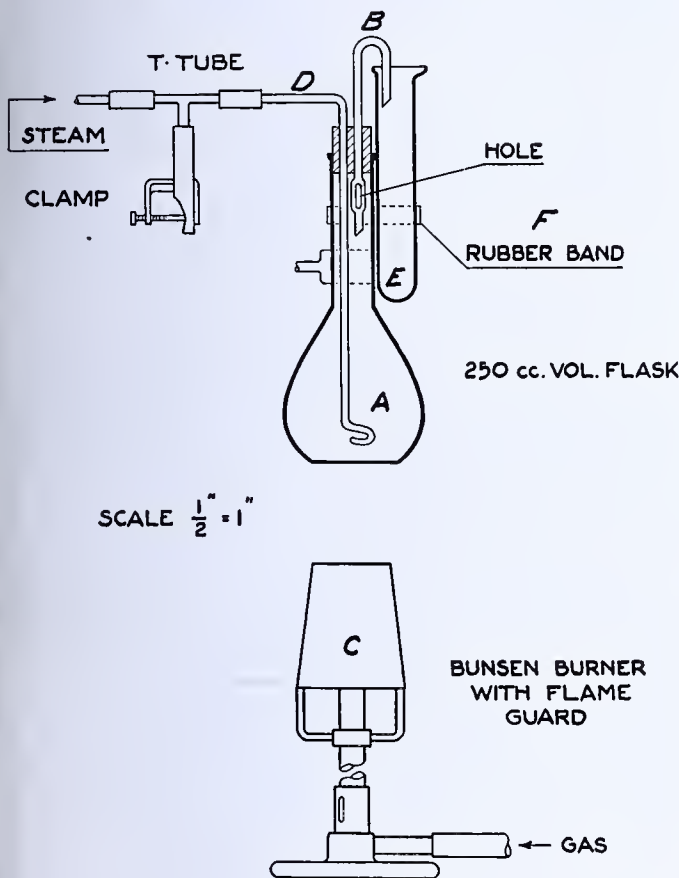


FIGURE 3. DIAGRAM OF APPARATUS

**PRIOR WASHING WITH COLD SOLVENT.** When 1- and 0.5-gram charges of superphosphates and triple superphosphates are digested directly with solvent, pH is not materially altered. Decided increase in pH is induced, however, by full charges of tricalcium phosphate and heavily ammoniated and mixed materials. Austin (3) and Jacob and Tremearne (14) have pointed out that prior aqueous washing is requisite to

TABLE II. EFFECT OF INCLUDED CITRATE UPON SOLVENT CAPACITY OF  $M$  AMMONIUM NITRATE DURING BOILING DIGESTION

Code <sup>a</sup>	Phosphatic Material	Total $P_2O_5$	Available $P_2O_5$		
			Neutral ammonium citrate <sup>b</sup>	Normal ammonium nitrate <sup>c,d</sup>	Citrated ammonium nitrate <sup>c,e</sup>
1060	Superphosphate	20.80	20.07	18.4	19.7
1066	Superphosphate	20.00	19.95	..	20.13
1087	Superphosphate	21.60	20.90	18.2	20.9
1378	Superphosphate	20.50	16.90	..	16.75
1337	Triple superphosphate	46.70	46.52	43.8	46.50
1338	Triple superphosphate	45.00	44.95	..	44.80
1368	Triple superphosphate	47.80	44.76	42.4	44.65
1415	Triple superphosphate	48.80	46.24	..	46.80
1518	Ammoniated superphosphate	47.60	45.80	42.0	47.0
1522	Mixed fertilizer	20.86	20.74	18.4	20.60
1526	Mixed fertilizer	16.90	16.78	16.2	16.40
..	Tricalcium phosphate	39.60	16.90	..	38.4

<sup>a</sup> Numbers are those of Bureau of Chemistry and Soils.  
<sup>b</sup> Official procedure.  
<sup>c</sup> 1-gram charges of standard superphosphates, 0.5-gram for concentrated materials.  
<sup>d</sup>  $M$  ammonium nitrate without citrate, otherwise as in <sup>c</sup>.  
<sup>e</sup>  $M$  ammonium nitrate-0.05  $M$  ammonium citrate, pH 4.2; prior leaching and boiling digestion for 15 minutes.

obtain maximal solvent action of neutral ammonium citrate in the analysis of acidulated materials by the official procedure. Prior leaching with cold solvent was therefore used to diminish the amounts of  $P_2O_5$  and salts so that the subsequent boiling digestion with solvent would be subject to less depression by pH change and common ion effect.

The  $P_2O_5$  removals effected by leaching acidic and basic phosphates with solvent are shown in Table III. Removals were in the range of 95 per cent for superphosphates, 85 per cent for mixed fertilizers, 60 to 90 per cent for ammoniated materials, 40 to 50 per cent for basic types, and about 30 per cent for slags and bone meals. Moreover, calcium sulfate was almost completely removed by the prior washing with solvent, whereas Jacob and Tremearne (14) have shown that only about 35 per cent is removed by aqueous leaching.

The comparisons of Table IV show the  $P_2O_5$  values obtained for experimental basic materials by the two steps of prior leaching and digestion with solvent, in comparison with direct digestion. The mean of the 12 values obtained by prior leaching with solvent was 92 per cent against 84 per cent for the direct digestions.

Aqueous washing of basic phosphatic materials that contain fluorides is conducive to the development of insolubility through hydrolysis and through formation of fluorapatite. This tendency is lessened, if not obviated, by the use of the acidic solvent for the prescribed leaching. Higher results for the leached ammoniated products can also be attributed



FIGURE 4. SINGLE ALL-GLASS EXPERIMENTAL UNIT, WITH SEPARATE OF STEAM INLET AND OUTLET OF DIGESTION FLASK



TABLE III. AVAILABLE  $P_2O_5$  FRACTION REMOVED FROM PHOSPHATIC MATERIALS BY 100-ML. COLD CITRATED AMMONIUM NITRATE LEACHINGS

Code	Material <sup>a</sup>	Available $P_2O_5$		
		In sample	In 100 ML. of Leachate	Fraction
		%	%	%
1060	Superphosphate	19.7	18.7	95
1378	Superphosphate	16.8	14.0	83
1368	Triple superphosphate	44.8	43.0	96
Ma	Ammoniated superphosphate	16.8	10.7	64
Mb	Ammoniated superphosphate	16.5	10.5	61
Mc	Ammoniated triple superphosphate	40.0	35.0	88
1508	Mixed fertilizer	8.8	6.3	72
1522	Mixed fertilizer	20.6	17.3	84
1523	Mixed fertilizer	10.3	8.8	85
1526	Mixed fertilizer	16.4	14.4	88
T-3	Basic slag	12.1	3.9	32
S-1	Raw bone	18.6	5.0	27
S-2	Steamed bone	18.2	6.8	37
J-1	Steamed bone	23.6	7.7	33
J-t	Dicalcium phosphate	50.2	22.1	44
J-t	Tricalcium phosphate	28.5	21.5	56
J	Ca hydroxyphosphate <sup>b</sup>	34.2	16.1	47
615	Ca fluorophosphate <sup>c</sup>	16.6	7.0	42

<sup>a</sup> 35-mesh fineness; 1-gram charges for all materials except triple superphosphate and di- and triphosphates, for which 0.5-gram charges were used.

<sup>b</sup> Supplied by K. D. Jacob, Bureau of Chemistry and Soils.

<sup>c</sup> A laboratory product.

TABLE IV. EFFECTIVENESS OF PRIOR LEACHING

(Excessively-limed and ammoniated laboratory-prepared superphosphates with cold citrated ammonium nitrate solution<sup>a</sup> in promoting  $P_2O_5$  removals by subsequent boiling extractions)

Code	Superphosphate Mixtures			Total $P_2O_5$	Available $P_2O_5$ Content Found	
	Type of superphosphate	Additions to Mixtures	Material Proportion		Prior leaching <sup>c</sup> and Direct nitrate boiling digestion without prior leaching <sup>b</sup>	subsequent boiling digestion with citrated ammonium nitrate <sup>b</sup>
			%	%	%	%
Ma	Standard	NH <sub>3</sub>	4.91	19.30	82.9	94.3
Mb	Standard	NH <sub>3</sub>	4.40	18.45	81.8	92.1
		Dolomite	10.00	...	...	...
Me	Standard	Dolomite	10.00	19.10	98.4	98.4
Mf	Standard	Dolomite	30.00	16.05	97.2	99.7
1168	Standard	NH <sub>3</sub>	8.70	19.40	69.5	84.5
1185	Standard	Ca(OH) <sub>2</sub> <sup>d</sup>	16.67	17.30	73.4	93.1
Mc	Triple	NH <sub>3</sub>	8.65	39.75	90.3	100.0
Md	Triple	NH <sub>3</sub>	7.94	37.50	91.3	97.6
		Dolomite	10.00	...	...	...
571	Triple	Limestone	30.00	44.70	79.4	80.5
573	Triple	Dolomite	30.00	41.40	90.6	93.7
576	Triple	NH <sub>3</sub>	12.40	43.70	79.2	86.6
580	Triple	NH <sub>3</sub>	7.96	24.60	79.3	88.6
		Gypsum	50.00	...	...	...

<sup>a</sup> M ammonium nitrate-0.05 M ammonium citrate, pH 4.2.

<sup>b</sup> Boiling digestion for 30 minutes; 1-gram charges for "standard" mixtures; 0.5-gram charges for triple mixtures.

<sup>c</sup> Washing with 100-ml. of solution noted in <sup>a</sup> by gravity. Leachate and boiled extract combined to 250 ml. for  $P_2O_5$  determinations.

<sup>d</sup> From slurry, 1 part Ca(OH)<sub>2</sub> and 5 parts of superphosphate; aged 1 week; dried at 45° C. (see 14, p. 280).

partly to substantial diminution of the common-ion effect during the subsequent digestion with solvent, an effect that will be considered further.

**SIZE OF CHARGE.** The data of Table V show values obtained by official procedure, and by direct digestions of 1- and 0.5-gram charges with a M ammonium nitrate solution that contained only a 0.025 M concentration of citrate, or one-half of that ultimately prescribed. The digestions were made without the preliminary leaching subsequently prescribed for the proposed procedure.

For the seven acidic materials, the official method gave values in accord with those obtained by the use of both 1- and 0.5-gram charges in the direct digestions with the nitrate solution. Values by the direct nitrate digestion of the 0.5-gram charges of the ammoniated materials exceeded those found for the 1-gram charges. It was evident that a prior leaching and a citrate concentration greater than 0.025 M would be required to assure adequate values when 1-gram charges of some ammoniated and basic materials are used.

In a supplemental series of eleven highly ammoniated and dolomite-treated products, five of superphosphate and six of triple superphosphate, 0.5- and 1.0-gram charges were analyzed by the official technic. The mean total  $P_2O_5$  content of the eleven materials was 29.4 per cent. The mean coefficient of availability by the official method was 84.7 per cent. When 0.5-gram charges were used, the corresponding mean by the official technic was 89.8 per cent, as against 92.5 per cent for the ultimate procedure with solvent.

**TRICALCIUM PHOSPHATES; SOLUBILITY BY AMMONIUM CITRATE AND BY PROPOSED PROCEDURE.** Since ammoniation and incorporation of calcic materials in superphosphates engender precipitated tricalcium phosphates and fluorapatite (15, 17, 18, 20, 23), the solubility of these phosphates is an important factor in the analysis of ammoniated materials. Values obtained by the conventional citrate digestions of three precipitated tricalcium phosphates, one hydroxyphosphate, and a synthetic fluorapatite were therefore compared with those obtained by the proposed procedure.

As shown in Table VI, citrate digestion gave only about 40 to 50 per cent of the  $P_2O_5$  content of c. p. tricalcium phosphates, as against a range of 82 to 96 per cent for solvent. If a tricalcium phosphate is of uniform composition, the fraction undissolved by citrate should have the same composition and evaluation as the substantially equivalent fraction that is not dissolved by the citrate digestion, unless a more basic and less soluble form is developed during the citrate digestion. The practically complete dissolving action of solvent therefore seems a more equitable measurement of the value of tricalcium phosphate and accords with the values found by collaborative plant-growth studies (8, 30, 31).

By both citrate and solvent digestions, the values for precipitated phosphates exceeded those for the hydroxyphosphate and fluorapatite. Granting that hydroxyapatite develops in commercially processed superphosphates, its solubility by the proposed procedure approaches that found for ordinary tricalcium phosphate.

The synthetic fluorapatite was the least soluble of the three phosphates in both citrate solution and solvent. The marked disparity in the values obtained for synthetic fluorapatite by the two methods was considerably diminished, however, when a 0.5-gram charge of fluorapatite was used in the citrate digestion. The solubility of synthetic fluorapatite will be considered further in a study of its mixtures with various proportions of di- and tricalcium phosphates.

TABLE V. INFLUENCE OF SIZE OF ANALYTICAL CHARGE UPON  $P_2O_5$  AVAILABILITY DETERMINATIONS

(M Ammonium nitrate-0.025 M ammonium citrate solvent)

Code	Phosphatic Material	Total $P_2O_5$	Available $P_2O_5$			
			By Neutral Ammonium Citrate Procedure	By Citrated Ammonium Nitrate Procedure	1-gram charge	0.5-gram charge
		%	%	%	%	%
1508	Mixed fertilizer	9.40	8.88	8.60	8.70	
1522	Mixed fertilizer	20.86	20.74	20.55	20.60	
1523	Mixed fertilizer	10.60	10.53	10.60	10.60	
1526	Mixed fertilizer	16.90	16.78	16.60	16.60	
1104	Wet mixed base goods	13.83	12.83	12.55	12.60	
1105	Wet mixed base goods	9.70	6.70	6.95	7.00	
1378	Standard superphosphate	20.50	16.90	17.30	17.40	
1168	Ammoniated superphosphate	19.40	13.80	13.30	16.60	
580	Ammoniated superphosphate	24.60	19.50	18.65	21.80	
Ma	Ammoniated superphosphate <sup>a</sup>	19.30	14.30	16.15	18.20	
Mb	Ammoniated superphosphate <sup>b</sup>	18.45	13.85	16.50	17.00	
J	Steamed bone meal	34.00	19.50	20.25	25.86	
J	Basic slag, low <sup>c</sup>	11.30	1.92	1.65	2.20	
J	Basic slag, high <sup>c</sup>	17.90	14.02	11.05	15.40	

<sup>a</sup> Straight ammoniated product aged 6 weeks at 54° C.

<sup>b</sup> Ammoniated product containing dolomite and aged 6 weeks at 54° C.

<sup>c</sup> Samples highly basic and gave strong ammoniacal odor when wetted with solvent.



TABLE VI. AVAILABLE  $P_2O_5$  CONTENT OF PRECIPITATED FORMS OF TRICALCIUM PHOSPHATE  
As determined by ammonium citrate digestion and by citrated ammonium nitrate digestion of proposed procedure)

Tricalcium Phosphate Type	Source	Total $P_2O_5$ %	P <sub>2</sub> O <sub>5</sub> Values by Digestions with—				Increase in Avail- ability by Citrated Ammonium Ni- trate Digestion			
			Neutral Ammonium Citrate <sup>a</sup>		Citrated Ammonium Nitrate <sup>b</sup>		As fraction of total		As fraction of total	
			Insolu- ble %	Actual %	Actual %	Actual %	As fraction of total %	As fraction of total %	Actual %	As fraction of total %
precipitated	J. T. Baker Co.	40.50	23.60	16.90 <sup>c</sup>	41.7	38.40	94.8	21.5	53.1	
	Baker & Adamson	40.00	19.50	20.50	51.3	38.40	96.0	17.9	44.7	
	Eimer & Amend	40.40	22.90	17.50	43.3	33.30	82.4	15.8	39.1	
hydroxyapatite <sup>d</sup>	Bureau of Chemistry and Soils	41.83	29.91	11.92 <sup>e</sup>	28.5	33.40	79.8	21.5	51.3	
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> - CaF <sub>2</sub>	Laboratory product <sup>f</sup>	37.60	29.50	8.10 <sup>g</sup>	21.5	13.80	36.7	5.7	15.2	

<sup>a</sup> Standard charge 1 gram per 100 ml. of solution, 1.09 sp. gr.

<sup>b</sup> Charge of 0.5 gram digested in 100 ml. of citrated ammonium nitrate solution after 100-ml. washing with cold solvent.

<sup>c</sup> Use of 0.5-gram charge gave 31.00 per cent.

<sup>d</sup> Supplied by K. D. Jacob.

<sup>e</sup> Use of 0.5-gram charge gave 17.17 per cent.

<sup>f</sup> Made by reaction between Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and CaF<sub>2</sub>.

<sup>g</sup> Use of 0.5-gram charge gave 12.20 per cent.

CALCIUM SULFATE AND CALCIUM FLUORIDE AS FACTORS IN CITRATE AND SOLVENT DIGESTIONS. Both calcium sulfate and calcium fluoride decrease the solvent capacity of ammonium citrate for tricalcium phosphate (13). Component calcium fluoride will also combine with tricalcium phosphate to form the less soluble fluorapatite during the official ammonium citrate digestion (17, 20). The influence of the sulfate and of the fluoride upon the capacity of the solvent was therefore studied in the four systems of Table VII.

Each mixture contained 0.5 gram of tricalcium phosphate and 0.1 gram of diammonium phosphate, with a total  $P_2O_5$  content of 21.6 per cent on the basis of a 1-gram charge of hypothetical material intended to simulate the phosphate makeup of a 1-gram charge of a highly ammoniated and reverted superphosphate devoid of fluorapatite. Immediately before analysis, sufficient CaSO<sub>4</sub>·2H<sub>2</sub>O was added to supply 30 per cent of SO<sub>3</sub> to a 1-gram charge. It has been pointed out that aqueous leaching leaves a major fraction of component sulfate to influence the solvent capacity of the citrate solution (14), whereas washing with solvent removes practically the entire sulfate content. That fraction of the sulfate addition that was unremoved by leaching exerted a heavier depression upon the solvent action of official citrate reagent, whereas no common-ion effect was induced in the digestion with solvent.

The additions of calcium fluoride supplied 1.6 per cent of fluorine and were also made immediately before the analyses of the phosphate mixtures. The added fluoride caused a decrease of 3.7 per cent in citrate-solubility, whereas the same addition plus calcium sulfate caused a further decrease of 5.8 per cent. These two decreases in citrate-solubility were twice those induced by the fluoride in the corresponding digestions with solvent. For the phosphate mixtures to which additions of calcium sulfate, calcium fluoride, and calcium sulfate plus calcium fluoride had been made, higher respective values of 1.5, 3.1, and 4.1 per cent were obtained by solvent.

Considered in connection with the data of Tables III and IV that show the extent and effect of removals of phosphatic components from basic fertilizers, the results of Table VII indicate that the analytical error attributable to formation of fluorapatite during ammonium citrate digestions is appreciable when the citrate is rendered alkaline by the dissolved mixtures of tri- and dibasic phosphates in the presence of fluorides (7, 20). Removal of basic phosphates by prior leaching with solvent tends to minimize the change in initial pH during the boiling digestion. Formation of fluorapatite cannot take place, however, at the initial pH of solvent. Any depressive effect upon the capacity of the boiling digestions to dissolve phosphates is therefore attributable primarily to the common-

ion effect induced by the dissolving of those compounds that are not removed by the prior cold leaching.

DI- AND TRICALCIUM PHOSPHATE MIXTURES WITH SYNTHETIC FLUORAPATITE; INFLUENCE OF PROPORTIONS AND SIZE OF CHARGE UPON SOLUBILITY IN SOLVENT. Values obtained for highly ammoniated and limed superphosphates, as well as concentrated single materials, such as tricalcium phosphates, are materially affected by variation in analytical charge, when the official technique is used (7, 8, 17, 20, 23, 28). Recognition of this fact led to decrease of charge to 1 gram

(30) and further decrease to 0.5 gram has been suggested.

Separate 0.5-gram charges of pure dicalcium phosphate are quickly and completely dissolved by solvent digestions, whereas a corresponding charge of precipitated tricalcium phosphate is almost completely dissolved. A 1-gram charge of an ammoniated superphosphate will not contain 0.5 gram of these phosphates, however, either singly or jointly. Failure to extract all of the engendered basic phosphates is therefore attributable to interference by other components and to formation of new compounds during the analytical procedure.

The amount of fluorapatite engendered in processed superphosphate is governed by proportions of tricalcium phosphate and fluorides, moisture, temperature, and period of aging. Extensive transition of tricalcium phosphate to the synthetic fluorapatite during processing can be considered primarily responsible for any incomplete recovery of  $P_2O_5$  from "reverted" materials that are subjected to the prescribed washing and digestion with solvent. The capacity of solvent to dissolve fluorapatite in association with variable proportions of di- and tricalcium phosphate was therefore studied.

TABLE VII. DEPRESSION IN  $P_2O_5$  AVAILABILITY

(Induced by additions of calcium sulfate and calcium fluoride immediately before analysis of a mixture of tricalcium phosphate and diammonium phosphate, as registered by official and citrated ammonium nitrate procedures)

Additions Made Immediately before Analysis of Phosphatic Mixtures <sup>a</sup>	Available $P_2O_5$ Values by Two Procedures—				
	Official citrate		Increased value by citrated ammonium nitrate		Depression Induced by Additions In citrated ammonium nitrate system
	%	%	%	%	%
None	19.9	21.2	1.3	..	..
CaSO <sub>4</sub> <sup>b</sup>	19.6	21.1	1.5	0.3	0.1
CaF <sub>2</sub> <sup>c</sup>	16.2	19.3	3.1	3.7	1.9
CaSO <sub>4</sub> + CaF <sub>2</sub> <sup>b,c</sup>	14.1	18.2	4.1	5.8	3.0

<sup>a</sup> Simulating an excessively ammoniated superphosphate; constant of 0.4 gram tricalcium phosphate and 0.1 gram diammonium phosphate, computed as 21.6%  $P_2O_5$  content of a 1-gram charge.

<sup>b</sup> Additions of 0.645 gram of CaSO<sub>4</sub>·2H<sub>2</sub>O, computed to supply 30 per cent SO<sub>3</sub> in a 1-gram charge.

<sup>c</sup> Constant of 0.035 gram, computed to supply 1.6 per cent fluorine in a 1-gram charge.

The mixtures of Tables VIII and IX were intended to simulate ammoniated materials containing variable proportions of synthetic fluorapatite and one of the two basic phosphates. The mixtures of Table VIII contained decreasing proportions of dicalcium phosphates and increasing proportions of synthetic fluorapatite, with a constant of 50 per cent of calcium sulfate. The mixtures of Table IX were identical with those of Table VIII, except that tricalcium phosphate was substituted for dicalcium phosphate. The proportions of the two phosphates present during the digestion were different from the initial proportions because of the variable



TABLE VIII. EFFECT OF PROPORTIONS OF DICALCIUM PHOSPHATE AND SYNTHETIC FLUOR-APATITE, AND OF CHARGE, UPON  $P_2O_5$ -AVAILABILITY

(Citratd ammonium nitrate procedure)

Phosphatic Components of 1-Gram Charge <sup>a</sup> By Weight					Available $P_2O_5$ Found				
CaHPO <sub>4</sub>		Fluor-apatite <sup>b</sup>		Total $P_2O_5$ %	Of Charge		Increase due to decreased charge	Of Total $P_2O_5$	
Gram	Gram	CaHPO <sub>4</sub> %	Fluor-apatite <sup>b</sup> %		1 gram %	0.5 gram %		1 gram %	0.5 gram %
0.5	0.0	26.70	0	26.70	26.70	26.70	0	100	100
0.4	0.1	20.56	3.76	24.32	20.60	24.00	3.4	85	99
0.3	0.2	15.42	7.52	22.94	16.90	22.30	5.4	74	97
0.2	0.3	10.28	11.28	21.56	12.60	19.20	5.0	63	90
0.1	0.4	5.14	15.04	20.18	10.20	16.30	6.0	51	81
0	0.5	0	18.80	18.80	6.90	10.80	3.9	37	57

<sup>a</sup> Constant 0.5-gram content of calcium sulfate.<sup>b</sup> A laboratory product.TABLE IX. EFFECT OF PROPORTIONS OF TRICALCIUM PHOSPHATE AND SYNTHETIC FLUOR-APATITE, AND OF CHARGE, UPON  $P_2O_5$ -AVAILABILITY

(Citratd ammonium nitrate procedure)

Phosphatic Components of 1-Gram Charge <sup>a</sup> By Weight					Available $P_2O_5$ Found				
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>		Fluor-apatite <sup>b</sup>		Total $P_2O_5$ %	Of Charge		Increase due to decreased charge	Of Total $P_2O_5$	
Gram	Gram	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> %	Fluor-apatite <sup>b</sup> %		1 gram %	0.5 gram %		1 gram %	0.5 gram %
0.5	0.0	20.25	0	20.25	19.25	19.90	0.65	95	98
0.4	0.1	16.20	3.76	19.96	14.00	18.30	4.30	70	93
0.3	0.2	12.15	7.52	19.67	11.70	16.10	5.00	59	82
0.2	0.3	8.10	11.28	19.38	9.85	13.80	3.95	51	71
0.1	0.4	4.05	15.04	19.09	8.50	12.50	4.00	45	65
0	0.5	0	18.80	18.80	6.90	10.80	3.90	37	57

<sup>a</sup> Constant 0.5-gram content of calcium sulfate.<sup>b</sup> A laboratory product.

amounts removed by the prior leaching to which the several mixtures were subjected.

The data of Table VIII show that, in absence of fluorapatite, 0.5- and 1-gram charges of dicalcium phosphates were dissolved completely by solvent. Of the total  $P_2O_5$  content supplied by the two phosphates, deficiencies of only 1 per cent and 3 per cent in recovery were induced by the fluorapatite in its 1 to 4 and 2 to 3 mixtures with dicalcium phosphate, when analytical charges of 0.5 gram were used. When 1-gram charges of the same two mixtures were used, the corresponding deficiencies were 15 and 26 per cent. Deficiencies in  $P_2O_5$  recovery were decreased to the minimal values of 37 and 57 per cent, respectively, for the 1- and 0.5-gram charges of the fluorapatite alone. But, in the mixture that contained 4 parts of CaHPO<sub>4</sub> of 100 per cent solubility, and one part of 57 per cent soluble fluorapatite, furnishing 84.5 and 15.5 per cent of the total  $P_2O_5$  content of 24.32 per cent, a recovery of 99 per cent was obtained by the use of the 0.05-gram charge.

Beginning with respective recoveries of 98 and 95 per cent from the 1- and 0.5-gram charges of c. p. tricalcium phosphate, the data of Table IX show the same order of values that were brought out for the dicalcium phosphate mixtures of Table VIII.

Tables VIII and IX show that the use of the smaller analytical charge gave a higher  $P_2O_5$  solubility for each mixture that contained synthetic fluorapatite and either di- or tricalcium phosphate. Recoveries decreased as fluorapatite proportions increased in both di- and tricalcium phosphate mixtures and the recovery from each tricalcium phosphate-fluorapatite mixture was less than the recovery from the corresponding dicalcium phosphate mixture.

Since the full charges of both di- and tricalcium phosphates—amounts beyond those to be encountered in the analysis of 1-gram charges of fertilizers—were completely dissolved by the digestions with solvent, any indications afforded by the proposed procedure as to undue retrogradation in ammoniated superphosphates should therefore be charged primarily to the formation of fluorapatite in the "reverted" material.

### Comparisons between Official and Proposed Procedures

SUPERPHOSPHATES AND MIXED FERTILIZERS. The comparisons of Table X show results for 20-mesh standard and "triple" superphosphates, mixed fertilizers, and ammoniated triple superphosphate and a c. p. tricalcium phosphate. The proposed procedure gave a somewhat higher value for the ammoniated triple superphosphate and 97 per cent solubility

TABLE X. AVAILABLE  $P_2O_5$  CONTENT OF SUPERPHOSPHATES AND MIXED FERTILIZERS

Code <sup>a</sup>	Phosphatic Material	Total $P_2O_5$ %	Available $P_2O_5$ by		Difference by Citratd Ammonium Nitrate %
			Official procedure %	Citratd ammo- nium nitrate <sup>b</sup> %	
1060	Standard superphosphate <sup>c</sup>	20.80	20.07	19.70	-0.37
1066	Standard superphosphate	20.00	19.95	20.13	+0.18
1087	Standard superphosphate	21.60	20.90	20.65	-0.25
1378	Standard superphosphate	20.50	16.90	16.75	-0.15
1522	Mixed fertilizer	20.86	20.74	20.60	-0.14
1526	Mixed fertilizer	16.90	16.78	16.40	-0.38
1337	Triple superphosphate <sup>d</sup>	46.70	46.52	46.50	-0.02
1338	Triple superphosphate	45.00	44.95	44.80	-0.15
1368	Triple superphosphate	47.80	44.76	44.65	-0.11
1415	Triple superphosphate	48.80	46.24	46.80	+0.56
..	Triple superphosphate (W. D. 31,847)	48.65	47.05	47.40	+0.35
1518	Ammoniated triple superphosphate	47.60	45.80	47.00	+1.20
1104	Base goods	13.83	12.83	12.52 <sup>e</sup>	-0.31
1105	Base goods	9.70	6.70	6.98	+0.28
1508	Mixed fertilizer	9.40	8.88	8.75 <sup>e</sup>	-0.13
1522	Mixed fertilizer	20.86	20.74	20.63	-0.11
1523	Mixed fertilizer	10.60	10.53	10.30	-0.23
1524	Mixed fertilizer	10.80	10.65	10.35	-0.30
1525	Mixed fertilizer	9.10	8.92	8.85	-0.07
1526	Mixed fertilizer	16.90	16.78	16.35	-0.43
1527	Mixed fertilizer	8.50	8.44	8.45	+0.01
R	Mixed fertilizer	17.80	15.60	16.38	+0.78
..	Tricalcium phosphate	39.60	16.90	38.40	+21.50

<sup>a</sup> Numbers are those of Bureau of Chemistry and Soils.<sup>b</sup> M ammonium nitrate-0.05 M ammonium citrate solution, pH 4.2; preliminary leaching and 15-minute boiling digestion.<sup>c</sup> 1-gram charges of standard products.<sup>d</sup> 0.5-gram charges of the concentrated materials.<sup>e</sup> Base goods and mixed fertilizers same as <sup>b</sup>, except boiling digestion period was 30 minutes.



or the precipitated tricalcium phosphate against 43 per cent by the ammonium citrate digestion.

In the 10 comparisons of Table X, fairly concordant results were obtained by official and proposed methods for the group of two "base goods" and eight mixed fertilizers, using 1-gram charges for both methods and a 30-minute period of boiling digestion with solvent. The maximal variation was a plus value of 0.78 per cent by the proposed procedure.

**EXPERIMENTAL BASIC MATERIALS.** Each of the 14 materials used in the comparisons of Table XI was an experimental mixture. Ten were ammoniated products, with or without dolomite, and four were unammoniated materials that contained either limestone or dolomite. In ten of the fourteen comparisons, the deviation was a plus value for solvent. All of the higher values in the 2.2 to 2.9 per cent range were for the highly ammoniated products. The three minus deviations of 0.45 to 0.50 per cent were for products that had been ammoniated beyond the limit found feasible in practice.

TABLE XI. AVAILABLE  $P_2O_5$  CONTENTS OF AMMONIATED AND BASIC SUPERPHOSPHATES

Code <sup>a</sup>	Treatment		Available $P_2O_5$ by			
	Ammoniated with $NH_3$ %	Additional %	Total $P_2O_5$ %	Official procedure %	Citrated ammonium nitrate <sup>b,c</sup> %	Difference by citrated ammonium nitrate %
69	2.5	None	20.60	18.90	18.80	-0.10
75	5.4	None	19.40	18.00	17.50	-0.50
68	8.7	None	19.40	13.80	13.30	-0.50
a	4.9	None	19.30	14.30	16.80	+2.50
0	8.0	None	24.60	19.50	19.05	-0.45
e	0	Dolomite, 10	19.10	18.10	18.50	+0.40
b	0	Dolomite, 30	16.05	15.10	15.60	+0.50
f	4.4	Dolomite, 10	18.45	13.90	16.50	+2.60
c	8.7	None	40.00	37.15	40.00	+2.85
6	12.4	None	43.70	39.70	40.65	+0.95
18	6.0	None	47.60	45.80	47.00	+1.20
1	0	Limestone, 30	44.70	34.40	36.15	+1.75
3	0	Dolomite, 30	41.40	37.80	38.60	+0.80
d	7.9	Dolomite, 10	37.50	34.09	36.30	+2.21

<sup>a</sup> Numerals those of Bureau of Chemistry and Soils; letters those of samples supplied by F. G. Keenen of du Pont Ammonia Experimental Station.

<sup>b</sup> 1-gram charges of standard products; 0.5-gram charges of triple superphosphate products.

<sup>c</sup>  $M$  ammonium nitrate-0.05  $M$  citrate solution; pH 4.2; preliminary ching and 30-minute period of boiling digestion.

**UREA-AMMONIA IMPREGNATED MATERIALS, CURED AT 2 TEMPERATURES.** Keenen and Morgan (16) have emphasized that development of citrate-insolubility during curing is materially increased by rise of temperature and the same effect has been found for mixtures of tricalcium phosphate and precipitated calcium fluoride (20). This factor was studied in the comparisons of Table XII. Three superphosphates and three mixed fertilizers were ammoniated by different quantities of urea-ammonia liquor. One-half of each of the ammoniated superphosphates was aged at 43° C. and the other at 54° C. for 38 weeks. The ammoniated mixed fertilizers were likewise divided and aged for 42 weeks.

In 11 of the 12 comparisons, the proposed procedure gave  $P_2O_5$  availabilities either higher or in accord with those obtained by the official method. Each of the six mixtures cured at the higher temperature showed a lower  $P_2O_5$  availability by both the official and proposed procedures. The mean of decreases induced by the 12° elevation was 1.93 per cent by the official procedure and only 1.25 per cent by the proposed procedure. No citrate-insolubility developed in a control series, however, when a fluoride-free triple superphosphate was ammoniated to a 12 per cent ammonia content and aged at 65° C. for 6 days.

The results of Table XII also register the effect of more extensive removal of sulfates and basic phosphates by prior washing with solvent. The basic phosphates, unremoved by aqueous leaching, vitiate the pH and solvent capacity of the citrate solution. Both hydrolysis of phosphatic components

and formation of fluorapatite occur during official analysis. In contrast, the smaller residues from solvent leaching influence the dissolving capacity of the boiling solvent primarily, if not solely, through diminished common-ion effect.

TABLE XII. COMPARISON OF AVAILABLE  $P_2O_5$  IN HEATED AMMONIATED SUPERPHOSPHATES<sup>a</sup>

Code	Type	Phosphate Fertilizer— Urea ammonia liquor additions Lb./ton		Available $P_2O_5$ — Citrated ammonium nitrate		
		Total $P_2O_5$ %	Official procedure %	Official procedure %	Citrated ammonium nitrate %	Difference by citrated ammonium nitrate %
1-A	Superphosphate <sup>b</sup>	200	19.0	16.35	16.93	+0.58
1-B	Superphosphate	200	19.0	12.40	14.00	+1.60
2-A	Superphosphate	170	19.5	17.30	17.55	+0.25
2-B	Superphosphate	170	19.5	14.20	15.45	+1.25
3-A	Superphosphate	140	20.0	19.50	19.10	-0.40
3-B	Superphosphate	140	20.0	18.05	18.78	+0.73
4-A	Mixed fertilizer <sup>c</sup>	90	9.5	8.86	8.83	-0.03
4-B	Mixed fertilizer	90	9.5	7.60	8.40	+0.80
5-A	Mixed fertilizer	120	9.5	7.26	8.48	+1.22
5-B	Mixed fertilizer	120	9.5	7.00	7.85	+0.85
6-A	Mixed fertilizer	90	13.75	13.45	13.35	-0.10
6-B	Mixed fertilizer	90	13.75	11.75	12.23	+0.48

<sup>a</sup> All values obtained by use of 1-gram charges.

<sup>b</sup> All of the superphosphates were aged 38 weeks; suffix A connotes aging at 43° C.; suffix B connotes aging at 54° C.

<sup>c</sup> All of mixed fertilizers were aged for 42 weeks; suffix A connotes aging at 43° C.; suffix B connotes aging at 54° C.

**ROCK PHOSPHATE SUPPLEMENTS; EFFECT UPON  $P_2O_5$  AVAILABILITY.** Rock phosphate is used as a fertilizer filler and it is claimed that a higher available  $P_2O_5$  content is thereby obtained by the official method. Analytical charges of the 10 fertilizers of Table XIII were supplemented by 10 per cent additions of substantially 300-mesh brown Tennessee rock phosphate and analyzed by the proposed procedure and by citrate digestions, with inclusion of filter (12).

If the  $P_2O_5$  solubility were a constant, when separate raw rock charges of 0.1 and 1.0 gram are subjected to boiling digestions with solvent, the available  $P_2O_5$  content of each of the 10 fertilizers should be increased 0.23 per cent by the rock supplements. But the smaller charges of raw rock, corresponding to the amounts encountered in analysis of rock-supplemented fertilizers, give slightly higher values when digested

TABLE XIII. EFFECT OF 10 PER CENT SUPPLEMENTS OF ROCK PHOSPHATE UPON AVAILABLE  $P_2O_5$  VALUES

Code	Phosphatic Material	Citrated Insoluble $P_2O_5$ <sup>a</sup> %	Available $P_2O_5$ Values <sup>b</sup> — Without rock supplements <sup>c</sup> With rock supplements <sup>d</sup>		
			Without rock supplements <sup>c</sup> %	With rock supplements <sup>d</sup> %	Increase due to rock supplements %
St.	Superphosphate	0.20	19.60	19.70	
			19.60	19.75	0.13
S-585	Superphosphate	0.35	20.20	20.25	
			20.30	20.30	0.03
1378	Superphosphate	3.60	16.65	16.95	
			16.85	17.05	0.25
4-A	Ammoniated superphosphate	0.64	8.75	9.20	
			8.90	9.15	0.35
4-B	Ammoniated superphosphate	1.90	8.45	8.35	
			8.35	8.55	0.05
5-A	Ammoniated superphosphate	1.24	8.45	8.50	
			8.50	8.60	0.08
5-B	Ammoniated superphosphate	2.50	7.85	8.00	
			7.85	8.00	0.15
1337	Triple superphosphate	0.18	46.50	46.80	
			46.50	46.90	0.35
1338	Triple superphosphate	0.05	44.80	45.10	
			44.60	45.20	0.45
S-44	Triple superphosphate	5.04	41.50	41.50	
			41.50	41.50	0.03
			41.40	41.60	

<sup>a</sup> By official method without supplements.

<sup>b</sup> By citrated ammonium nitrate, prior washing.

<sup>c</sup> Constant charge of 1 gram for superphosphate and 0.5-gram for triple superphosphates.

<sup>d</sup> Constant charge of 1 gram for superphosphate and 0.5-gram for triple superphosphates plus a constant 10 per cent supplement of rock phosphate.



TABLE XIV. AVAILABLE  $P_2O_5$  CONTENT OF BONE MEALS  
(Determined by digestions with neutral ammonium citrate and with citrated ammonium nitrate)

Code <sup>a</sup>	Type of Bone <sup>b</sup>	Total $P_2O_5$	Neutral Ammonium Citrate <sup>c</sup>	Citrated Ammonium Nitrate <sup>d</sup>	Difference by Citrated Ammonium Nitrate
		%	%	%	%
S1	Raw	21.00	13.08	18.55	+5.47
S2	Steamed	23.40	14.68	18.15	+3.47
J1	Steamed	34.00	19.50	23.65	+4.65

<sup>a</sup> Numerals are those of producers.  
<sup>b</sup> Constant charges of 1 gram.  
<sup>c</sup> Official 1.09 sp. gr. solution; 1-hour digestion period at 65° C., 9-cm. filter included.  
<sup>d</sup> *M* ammonium nitrate-0.05 *M* citrate solution; pH 4.2; preliminary leaching and 30-minute boiling digestion period.

TABLE XV. AVAILABLE  $P_2O_5$  IN CALCINED (DEFLUORINATED) ROCK PHOSPHATES

Code <sup>a</sup>	Total $P_2O_5$ <sup>b</sup> %	Available $P_2O_5$			Insoluble $P_2O_5$	
		By ammonium citrate digestion <sup>b</sup> %	By citrated ammonium nitrate digestion <sup>c</sup> %	Difference by citrated ammonium nitrate digestion %	By am- monium citrate digestion %	By citrated ammonium nitrate digestion %
1322	34.42	27.16	29.2 29.2 29.6	+2.24	6.26	4.02
1325	33.97	22.21	25.8 26.0	+3.69	11.76	8.07
1327	34.21	29.46	32.0 31.6	+2.34	4.75	2.41
1374	35.17	31.26	33.0 33.2	+1.84	3.91	2.07
1375	35.09	32.52	34.4 34.0	+1.68	2.57	0.89
1478	37.25	33.52 <sup>d</sup>	35.2 35.2	+1.68	3.73	2.05

<sup>a</sup> Numbers are those of Bureau of Chemistry and Soils.  
<sup>b</sup> Values for total and citrate-soluble  $P_2O_5$  were furnished by K. D. Jacob, Bureau of Chemistry and Soils.  
<sup>c</sup> Using prescribed 0.5-gram charge.  
<sup>d</sup> Charges of 0.25 and 0.5 gram gave respective values of 34.4 and 34.4 per cent.

with solvent. The supplements, therefore, impart a greater  $P_2O_5$  value than the one indicated by a separate analysis of a 1-gram charge of raw rock. To a more marked extent the same is true for citrate digestions. In six of the ten comparisons, however, the resultant increases were less than the analytical tolerance of 0.2 per cent. The mean increase in  $P_2O_5$  availability induced by the raw rock additions, representative of approximately 200 pounds per ton, was 0.19 per cent for the ten fertilizers.

But when present as a supplement in ammoniated super phosphates, the solubility of raw rock in solvent is decreased by the protective effect of concomitant occurrences of the engendered basic phosphates. Substantial residues of undecomposed rock phosphate, such as the 5 per cent citrate insoluble  $P_2O_5$  content of the triple superphosphate, S-44 likewise decrease the action of solvent upon added raw rock

Available  $P_2O_5$  by Citrate and Solvent Digestion

BONE MEAL. Determination of citrate-soluble  $P_2O_5$  in bone meal is not prescribed specifically in the methods of A. O. A. C. This material can be considered, however, a "nonacidulated samples other than basic slag" (1, p. 11). Table XIV shows a mean solubility of 60 per cent by citrate digestions against 77 per cent by the proposed procedure.

CALCINED (DEFLUORINATED) ROCK PHOSPHATE. Analysis of this relatively new product is not prescribed specifically by the A. O. A. C. methods. From collaborative studies Ross and Jacob (31) concluded, however, that the ammonium citrate digestion, with included filter, is applicable for the evaluation of calcined phosphates.

Table XV shows that the proposed procedure gave  $P_2O_5$  values of from 1.68 to 3.69 per cent beyond those found by citrate digestions. The mean total  $P_2O_5$  content of the six calcined phosphates was 35.02, of which 83.8 per cent was available by the citrate digestion and 90.2 per cent by boiling digestion with solvent.

FUSED PHOSPHATE ROCKS; INFLUENCE OF PARTICLE SIZE. Particle size exerted a marked effect upon the solubility of the calcined materials of Table XVI. Decrease in particle size gave greater solubility by both citrate and solvent. There was a much greater spread, however, between the values found by citrate digestions for coarsest and finest separates.

The solvent gave the higher  $P_2O_5$  value in each of the 10 comparisons. Reasonable concordance was shown, however, by citrate and solvent digestions of the finer separates. The mean difference between citrate values for 50-mesh and 325 mesh separates was 10.92 per cent, as against 5.5 per cent for digestion with solvent. The mean of values obtained by solvent for the rocks in the 22 to 30 per cent range was 2.1 per cent more than the mean value by citrate digestions.

Most of the respective differences in  $P_2O_5$  values by the two solvents are less than the variations induced by a mer-

TABLE XVI. AVAILABLE  $P_2O_5$  CONTENT OF FUSED TENNESSEE ROCK PHOSPHATES

Type	Analytical Charge Mesh	P <sub>2</sub> O <sub>5</sub> Dissolved by			
		Citrate digestion <sup>a</sup>	Citrated ammonium nitrate digestion <sup>b</sup>	Difference by citrated ammonium nitrate digestion	
			Gram	%	%
Fused brown No. 256, quenched	0.5	50-100	19.72(20.60)	23.2	+3.48
		100-200	23.41(26.10)	26.5	+3.09
		<200	27.79(28.85)	29.3	+1.51
		<325	29.62	30.0	+0.38
Fused brown	0.5	50-100	17.37(19.50)	25.1 <sup>c</sup>	+7.73
		100-200	24.50(25.10)	28.3	+3.80
		<200	26.50(26.00)	28.8	+2.30
		<325	27.25(27.50)	28.8	+1.55
Fused white	0.5	50-100	16.33(19.85)	23.50	+6.17
		100-200	22.60(24.60)	27.80	+5.20
		<200	27.60(28.60)	28.50	+0.90
		<325	29.30(29.10)	29.50	+0.20

<sup>a</sup> Ammonium citrate determinations, except bracketed values, were made with official citrate solution upon 1-gram charges, 1-hour digestion at 65° C. with filter included; bracketed values were obtained by use of 0.5-gram charges, filter included.  
<sup>b</sup> Prior washing and steam digestion with *M* ammonium nitrate-0.05 *M* ammonium citrate solution, pH 4.2.  
<sup>c</sup> When the four units of this series were duplicated with inclusion of 9-cm. filter, practically identical results were obtained.



mechanical variation in analytical technic of citrate digestion. The results of 21 collaborators showed a mean deviation of .51 per cent  $P_2O_5$  as the effect of a macerated 9-cm. filter in citrate digestions of 80-mesh material (31). A macerated filter in the steam digestion of leached residues is an integral feature of the proposed procedure, although presence of filter apparently exerts no influence upon the values obtained by the proposed procedure. Practically identical values were obtained for ammoniated superphosphates, steam bone, and rock phosphate, with and without an included macerated filter. The bracketed figures of Table XVI represent the values obtained by citrate digestions of 0.5-gram charges, instead of the customary 1-gram charge. The smaller charge gave a higher value in eleven instances. Nevertheless, with one exception, the values obtained by citrate digestion of the smaller charge were considerably less than those obtained by solvent. This was particularly true for the coarser particles. It is obvious that the fineness of fused rock is an important factor in its evaluation by chemical procedure.

TABLE XVII. AVAILABLE  $P_2O_5$  CONTENT OF BASIC SLAGS

Determined indirectly by digestions with neutral ammonium citrate and directly with citrated ammonium nitrate)

Code <sup>a</sup>	Type of Slag	Grade	Fluoride used in fluxation	Total $P_2O_5$ %	Available $P_2O_5$ by <sup>b</sup>		Difference by Citrated Ammonium Nitrate
					Neutral ammonium citrate <sup>c</sup> %	Citrated ammonium nitrate <sup>d</sup> %	
T1	Low	...	...	9.20	6.95	6.80	-0.15
T2	Low	Yes	...	8.40	4.90	5.36	+0.46
T3	High	No	...	13.00	11.88	12.10	+0.22
J1	Low	Yes	...	11.30	1.92	1.95	+0.03
J2	High	No	...	17.90	14.02	14.65	+0.63
S1	High	...	...	18.50	14.50	14.50	0

<sup>a</sup> Numerals are those of producers.

<sup>b</sup> Constant charge of 1 gram.

<sup>c</sup> Official 1.09 sp. gr. solution; 1-hour digestion period at 65° C.

<sup>d</sup>  $M$  ammonium nitrate-0.05  $M$  citrate solution; pH 4.2; preliminary leaching and constant boiling-digestion period of 30 minutes.

**BASIC SLAG.** The citrate and solvent digestions of Table VII gave fairly concordant values for the 6 basic slags whose total  $P_2O_5$  content ranged from 9.2 to 18.5 per cent. The maximal variation of plus 0.46 per cent by solvent digestion is only about one-fifth of the mean variation of results of collaborators for citrate digestion with and without filter paper (31). Thus, the variation induced by mere inclusion of a macerated filter in citrate digestion greatly exceeded the maximal difference found in the several comparisons of citrate and solvent digestions. Ross and Jacob (31) have also shown that citrate digestions and the official digestion with per cent citric acid (1) gave comparable results for basic slags. Both citrate and solvent register diminished solubility attributable to fluorspar used in the fluxation of two of the slags.

**RAW ROCK PHOSPHATES.** Table XVIII embodies 24 comparisons between neutral citrate and solvent digestions of raw rock phosphates. Each comparison showed lower result by solvent, although differences not exceeding 0.25 per cent were found in 8 of the 24 comparisons. Considerable variations in  $P_2O_5$  values are obtained for a given raw phosphate in duplications of citrate digestions, whereas repetitions of digestions with solvent give satisfactory concordance. Both solvents gave exceedingly low values for the Ontario apatite.

**RAW ROCK PHOSPHATES; INFLUENCE OF pH VALUE UPON COMPARATIVE SOLVENT CAPACITIES OF THE CITRATE AND SOLVENT.** Since the ammonium citrate and solvent prescribed by the official and the proposed procedures are, respectively, neutral and acidic, the point arises as to the effect of pH upon the solvent capacities of the citrate and solvent solutions. The analyses of Table XIX show values obtained from 1-gram charges of raw rocks by digestions with solvent and by digestions with each of two ammonium citrate solu-

TABLE XVIII. AVAILABLE  $P_2O_5$  CONTENT OF ROCK PHOSPHATES

Rock Phosphate			$P_2O_5$ Dissolved		Difference by nitrate digestion
Type	Source	Sample No. <sup>a</sup>	By citrate digestion and washing <sup>b</sup>	By citrated ammonium nitrate digestion <sup>c</sup>	
Brown rock	Tenn.	587	2.17	1.75	-0.42
	Tenn.	906	2.06	2.05	-0.01
	Tenn.	908	2.39	2.00	-0.39
Raw brown	Tenn.	(50-100)	2.50	2.15	-0.35
	Tenn.	(100-200)	2.45	2.25	-0.20
	Tenn.	(<200)	3.60	2.55	-1.05
	Tenn.	(<325)	3.30	2.55	-0.75
White rock	Tenn.	1031	3.55	3.35	-0.20
	Tenn.	1048	2.70	2.40	-0.30
Blue rock	Tenn.	449	2.40	1.68	-0.72
	Tenn.	930	1.97	1.55	-0.42
Hard rock	Florida	434	4.08	2.90	-1.18
	Florida	932	2.99	2.73	-0.26
Soft rock	Florida	1091	3.97	3.23	-0.74
Land pebble	Florida	439	3.72	...	...
Waste pond	Florida	915	2.63	2.53	-0.10
Land rock	S. C.	1138	4.85	3.20	-1.65
	S. C.	1139	5.17	3.20	-1.97
Rock	Idaho	454	2.99	1.85	-1.14
	Idaho	973	3.53	1.85	-1.68
	Montana	1252	1.65	1.40	-0.25
	Wyoming	948	1.44	0.65	-0.79
Apatite	Ontario	..	0.70	0.55	-0.15
Colloidal phosphate	Florida	..	2.72	2.50	-0.22

30-minute digestion with solvent without prior leaching; 1-gram charges.

<sup>a</sup> Numbers are those of Bureau of Chemistry and Soils, *Tech. Bull.* 364 (1933); four separates of Tennessee brown rock prepared locally.

<sup>b</sup> 1-hour digestion in solution of 1.09 sp. gr. at 65° C.; residue transferred and washed with ammonium citrate to minimize peptization of colloidal material.

<sup>c</sup> 1-hour steam injection agitation in  $M$  ammonium nitrate-0.05  $M$  ammonium citrate, pH 4.2.

tions. One citrate solution was neutral and the other had a pH identical with that of solvent. In each case the lowest of the three values found for the 4 raw rocks was obtained by solvent. Values by the neutral citrate and the solvent were comparable in three cases; but when pH of the citrate was lowered to 4.2, its solvent capacity was increased threefold (25, 26, 27, 29). The acidity of solvent is apparently not the primary reason for its greater capacity to dissolve the basic types of orthophosphates.

**CALCIUM METAPHOSPHATE.** Four 200-mesh Wilson Dam products of reported composition (19) were used for the comparisons of Table XX. Concordance for the values obtained

TABLE XIX. AVAILABILITY OF  $P_2O_5$  CONTENT OF ROCK PHOSPHATES

(Neutral ammonium citrate, acidified ammonium nitrate, and citrated ammonium nitrate digestions)

Code <sup>a</sup>	Source and Type of Raw Rock	Available $P_2O_5$ by <sup>b</sup>		
		Ammonium at pH 7.0	Citrate <sup>c</sup> at pH 4.2	Citrated ammonium nitrate, pH 4.2
908	Tenn., brown	2.39	8.32	2.30
932	Fla., hard	2.99	8.49	2.73
454	Idaho	2.99	7.99	1.93
1252	Montana	1.65	5.90	1.40

<sup>a</sup> Numbers are those of Bureau of Chemistry and Soils.

<sup>b</sup> Constant charge of 1 gram.

<sup>c</sup> Filter paper present during digestion with both of the citrate solutions.

TABLE XX. AVAILABLE  $P_2O_5$  CONTENT OF WILSON DAM CALCIUM METAPHOSPHATES

Code	Metaphosphate <sup>a</sup> Total $P_2O_5$ %	Available $P_2O_5$	
		Ammonium citrate <sup>b</sup> %	Citrated ammonium nitrate <sup>c</sup> %
443-A	63.5	63.1	61.3
443-B	65.0	64.1	64.3
274	64.9	64.3	64.8
275	62.8	57.8	58.3

<sup>a</sup> 200-mesh; for compositions of the 4 products, see (5).

<sup>b</sup> 1-gram charge.

<sup>c</sup> 0.5-gram charge.



by citrate and solvent digestions of the 200-mesh materials was about the same as that generally obtained from duplications of the citrate digestion. The upper limit for permissible particle size of the analytical charges of "glassy" metaphosphate was not determined, nor did the comparisons embrace commercial fertilizers containing admixtures of metaphosphates.

The prescribed boiling digestion with solvent hydrolyzed only about one-half of the dissolved metaphosphate and the proposed procedure therefore stipulates that the analytical aliquot be heated with nitric acid before the analytical molybdate precipitation.

### Advantages of Proposed Procedure

1. Simplicity, rapidity, reagent economy, and accuracy consonant with that of the official method for superphosphates and acidic fertilizers.
2. A single, easily made, and inexpensive solvent.
3. One  $P_2O_5$  determination for each fertilizer.
4. Applicability, with minor variations, to all commercial phosphatic fertilizers.
5. Maintenance of near-constancy in pH of solvent throughout digestions.
6. Minimal interference of common-ion effect upon solubility of phosphates in the analytical systems.
7. Elimination of error introduced by hydrolysis and by the formation of fluorapatite, which occurs during official aqueous leaching and citrate digestion of ammoniated and limed superphosphates.
8. No difficulty in obtaining clear filtrates.
9. Higher, more uniform, and readily duplicated values for tricalcium phosphates.
10. Values more in accord with those known to reside in calcined rocks and fused rocks.
11. Less variation incident to particle size of both raw and calcined rock phosphates.
12. Less enhancement in availability values for fertilizers carrying additions of raw rock.
13. Insoluble  $P_2O_5$ , if required, can be determined rapidly by the difference between total and available values. The two determinations can be carried out simultaneously.
14. Elimination of noxious fumes incident to digestion of insoluble residues.

### Summary and Conclusions

Direct determination of available  $P_2O_5$  is prescribed by use of solvent— $M$  ammonium nitrate— $0.05 M$  ammonium citrate, pH of 4.2—from which  $P_2O_5$  is precipitated during cold agitation.

**STIPULATIONS.** One-gram charges for standard acidic and ammoniated fertilizers, bones, slags, and raw rock; 0.5-gram charges for concentrated products of high availability; cold leaching with solvent, except for raw rocks; digestion of leached residue in solvent, with current of steam; combination of leachate and digestate into one solution for  $P_2O_5$  determination.

**STEAM DIGESTION.** Instantaneous purging of ammonia from solvent digestions of basic phosphates gave constancy of pH and complete solubility, whereas rise in pH and partial solvent action occurred in boiled digestions.

**INCLUSION OF CITRATE** in the ammonium nitrate solution was found to be essential, the citrate concentration being only one-ninth of that of the official citrate extractant.

**PRIOR WASHING WITH SOLVENT** effected  $P_2O_5$  removals in the range of 30 per cent for basic materials to 98 per cent for superphosphates; calcium sulfate was almost completely removed.

**SUPERPHOSPHATES.** Practically identical  $P_2O_5$  values by official and proposed procedures.

**MIXED FERTILIZERS.** The two procedures gave concordant values for acidic types.

**AMMONIATED COMMERCIAL PRODUCTS.** Higher values by proposed procedure.

**AMMONIATED AND HEAVILY LIMED EXPERIMENTAL MIXTURES.** In most cases somewhat higher  $P_2O_5$  values by proposed procedure.

**PRECIPITATED TRICALCIUM PHOSPHATES.** Much higher values by solvent.

**HYDROXYAPATITE.** Higher values by solvent.

**SYNTHETIC FLUORAPATITE.** Low solubility by solvent.

**CALCIUM SULFATE AND CALCIUM FLUORIDE EFFECT.** Depressions of  $P_2O_5$ -solubility induced in official digestions of mixtures

of diammonium and tricalcium phosphates were about twice those induced in digestions with solvent.

**DICALCIUM AND TRICALCIUM PHOSPHATE PROPORTIONS IN MIXTURES WITH SYNTHETIC FLUORAPATITE.** Variable proportions in the 2-phosphate systems and size of charge were reflected by the extent of  $P_2O_5$  recoveries by solvent digestions.

**ROCK PHOSPHATE ADDITIONS.** Ten per cent additions to superphosphates and ammoniated superphosphates caused small increase in available  $P_2O_5$  by the proposed procedure.

**BONE MEAL.** Solubility by the proposed procedure considerably greater than by citrate digestions.

**CALCINED ROCK PHOSPHATES.** Solvent digestions gave value 0.9 to 8.1 per cent greater than those obtained by citrate digestions, with included filter.

**FUSED ROCK PHOSPHATES.** Solubility in solvent exceeds that in citrate. In 50- to 325-mesh range, decrease in particle size caused greater values by both citrate and solvent digestions, with less spread in values by solvent.

**BASIC SLAGS.** Citrate and solvent digestions gave somewhat comparable values.

**RAW ROCK PHOSPHATES.** Solubility in solvent somewhat less than in neutral ammonium citrate; dissolving action of citrate solution of pH 4.2 was threefold that of neutral solution.

**CALCIUM METAPHOSPHATES.** Concordant values by citrate and solvent digestions only on finely ground material.

### Acknowledgment

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# The Proximate Analysis of Gasoline

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MANY methods have been devised for determining the chemical group composition of gasolines. Excellent reviews of these methods have been published by Faragher, Morrell, and Levine (3), Schildwächter and Martin (14), Manning and Shepherd (7), Kester and Pohle (5), and others (6). Both the early methods reviewed in these papers and the more recent procedures, including those of Minter (10), Barriere and Lautie (2), Marder (8), Vlugter (15), and Curtz and Headington (6), have the general disadvantage of being too cumbersome for the rapid routine analysis of the small amounts of gasoline most conveniently obtained from small-scale laboratory operations. In addition, many of the methods are of doubtful accuracy. It has been desirable for the authors' work to develop a method which combined rapidity, simplicity, and reasonable accuracy with adaptability to the analysis of relatively small samples (100 to 300 cc.).

The method finally adopted involves the separation of the gasoline into fractions in which the hydrocarbons of each chemical group contain approximately the same number of carbon atoms; the determination of the olefins in each fraction by the bromate-bromide method; the determination of total olefins and aromatics in each fraction by a single extraction at 0° C. with fuming sulfuric acid containing 25 per cent of sulfur trioxide; and the estimation of the naphthene content of the residue from the acid extraction by its refractive index.

## Fractionation

The fractionation may be carried out with any small laboratory fractionating column having a low holdup and a frac-

tionating efficiency equivalent to 5 to 10 theoretical plates. The column illustrated in Figure 1 has been found especially useful for this purpose. When the gasoline contains C<sub>4</sub> hydrocarbons, the dry ice condenser is used and C<sub>4</sub> can be refluxed so that a clean separation between C<sub>4</sub> and C<sub>5</sub> is made. The column is a combination of the head described by Marshall (9) and the type of body described by Podbielniak (13).

The gasoline is separated into fractions as follows:

Fraction	Boiling Point ° C.	Constituents
1 (C <sub>4</sub> ) <sup>a</sup>	10-40	C <sub>4</sub> paraffins, olefins
2 (C <sub>5</sub> )	40-70	C <sub>5</sub> , C <sub>6</sub> naphthenes C <sub>6</sub> paraffins, olefins
3 (C <sub>7</sub> )	70-100	C <sub>6</sub> naphthenes, aromatics C <sub>7</sub> paraffins, olefins
4 (C <sub>8</sub> )	100-125	C <sub>7</sub> naphthenes, aromatics C <sub>8</sub> paraffins, olefins, naphthenes
5 (C <sub>9</sub> )	125-150	C <sub>8</sub> naphthenes, aromatics C <sub>9</sub> paraffins, olefins, naphthenes
6 (C <sub>10</sub> )	150-175	C <sub>9</sub> aromatics C <sub>10</sub> paraffins, olefins, naphthenes
7 (C <sub>11</sub> )	175-195	C <sub>10</sub> aromatics C <sub>11</sub> paraffins, olefins, naphthenes

<sup>a</sup> Because only paraffins and olefins are present in this fraction, the olefin determination alone is necessary, the paraffins being obtained by difference.

This fractionation separates the mixture into fractions in which the constituents of each chemical group have about the same molecular weight. Because of the overlapping of the boiling points of some of the isomers and imperfect fractionation, however, each fraction will usually contain some hydrocarbons which belong to the next lower and next higher boiling fractions.

Before each cut is made the column is run under total reflux for 5 to 10 minutes to be sure that the cut temperature

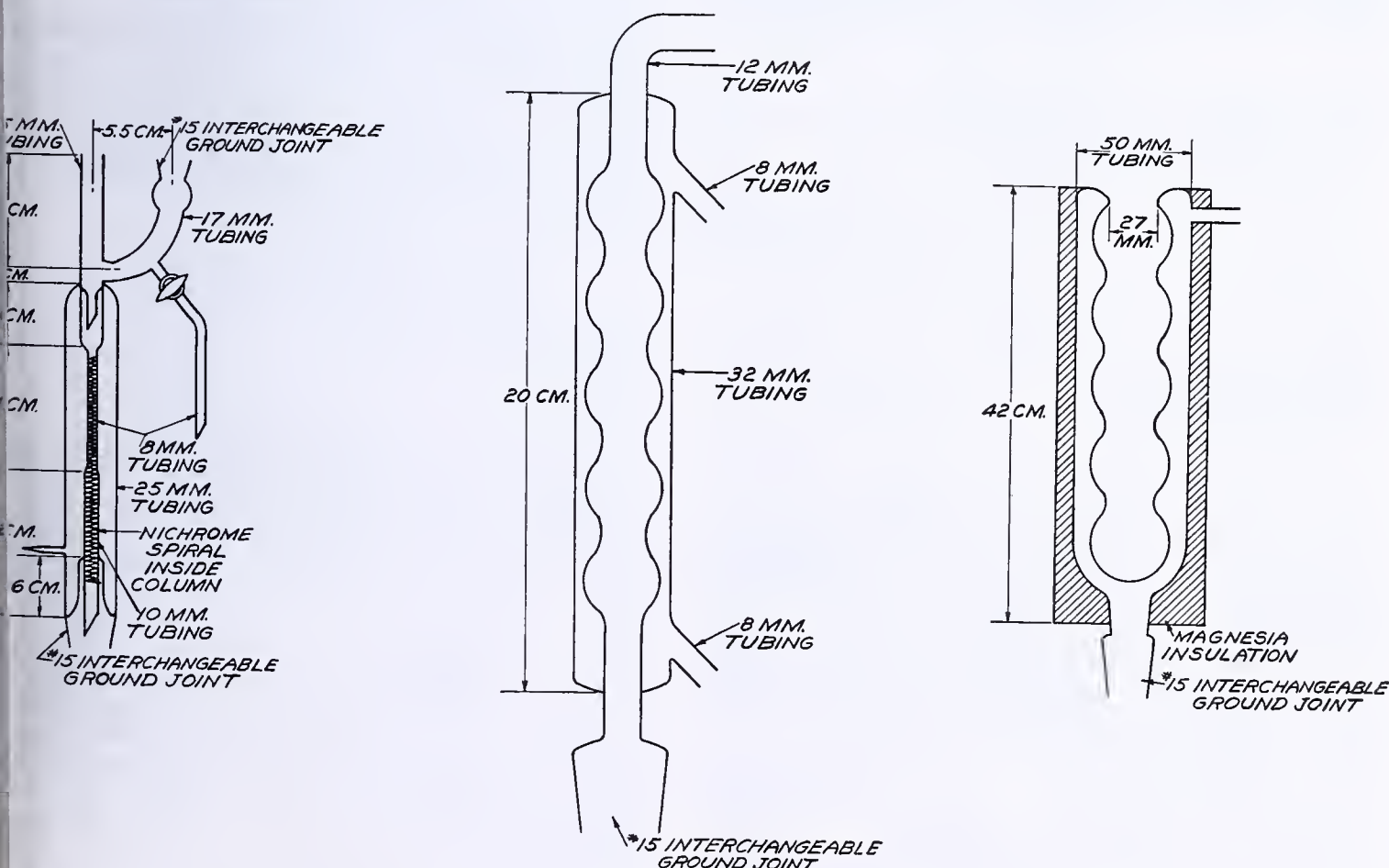


FIGURE 1. FRACTIONATING COLUMN, WATER CONDENSER, AND DRY ICE CONDENSER



has been reached. If the temperature drops under total reflux, more distillate is removed until the cut temperature is again reached. Alternation between total reflux and a slow distillation is continued until the temperature does not fall with the column running at total reflux.

### Olefin Determination

The olefins are determined by a modification of the methods of Francis (4) and Mulliken and Wakeman (11).

**REAGENTS.** C. P. carbon tetrachloride, 10 per cent sulfuric acid, a solution containing 15 per cent of c. p. potassium iodide, a 1 per cent solution of "soluble starch" containing 0.1 per cent of zinc chloride as a preservative, a solution containing 13.92 grams of potassium bromate (c. p.) and 50 grams of potassium bromide (c. p.) per liter (this solution is 0.5 *N*), and a 0.2 *N* solution of sodium thiosulfate.

### Procedure

Mix 10 cc. of carbon tetrachloride and 10 cc. of 10 per cent sulfuric acid in a 250-cc. glass-stoppered Erlenmeyer flask and chill thoroughly in ice. Add to this mixture 1 cc. of the hydrocarbon measured at a known temperature. The most volatile fractions must be precooled before pipetting. Mix the sample in the carbon tetrachloride by shaking and cool again in ice. From a buret add 1 cc. of 0.5 *N* bromate-bromide solution. Shake vigorously and quickly immerse in ice. Continue periodic shaking and immersion until the yellow bromine color disappears. Continue to add 1-cc. portions of the bromate-bromide solutions in this manner until a permanent yellow color is observed in the carbon tetrachloride. (The bromate-bromide solution may be added in 2- to 5-cc. portions when it is known that the sample is quite unsaturated.) For each 10 cc. of bromate-bromide solution used add 5 cc. of 10 per cent sulfuric acid. When the yellow color no longer disappears, add 5 cc. of 15 per cent potassium iodide and titrate with 0.2 *N* sodium thiosulfate. Add the starch indicator when the color of the iodine in the carbon tetrachloride has almost disappeared.

Until the potassium iodide is added it is imperative to keep the mixture as near to 0° C. as possible, in order to minimize substitution reactions and prevent loss of bromine vapor.

The bromine number, *B*, is calculated from the formula

$$B = \frac{8}{d} (N_1 V_1 - N_2 V_2)$$

*N*<sub>1</sub> = normality of bromate-bromide solution

*V*<sub>1</sub> = cc. of bromate-bromide solution used

*N*<sub>2</sub> = normality of thiosulfate solution

*V*<sub>2</sub> = cc. of thiosulfate solution used

*d* = density of hydrocarbon sample at temperature used

The weight per cent, *W*, of olefins may be calculated from the equation

$$W = \frac{B}{160} M$$

*W* = weight per cent olefins

*B* = bromine number

*M* = molecular weight of olefins in fraction (70 for C<sub>6</sub>, 84 for C<sub>6</sub>, etc.)

### Determination of Aromatics

**PROCEDURE.** Pipet 10 cc. of the sample into a modified Babcock bottle, and chill thoroughly in ice water. Gradually add, little by little, three volumes of fuming sulfuric acid (25 per cent sulfur trioxide), shaking the bottle vigorously after each addition, but keeping it immersed in ice water. After all the acid has been added, and a smooth emulsion achieved, centrifuge the mixture at 1000 r. p. m. for 2 or 3 minutes or allow it to stand until a clean separation into two layers is effected. The unabsorbed volume is read at the same temperature (either 0° or room temperature) as was used in measuring the sample.

The volume of aromatics is the difference between the total amount absorbed and the volume of olefins present.

**DETERMINATION OF NAPHTHENES AND PARAFFINS.** Wash the residue from the sulfuric acid absorption in a small separatory funnel, twice with water and once with a 10 per cent sodium carbonate solution. Dry it with anhydrous potassium carbonate

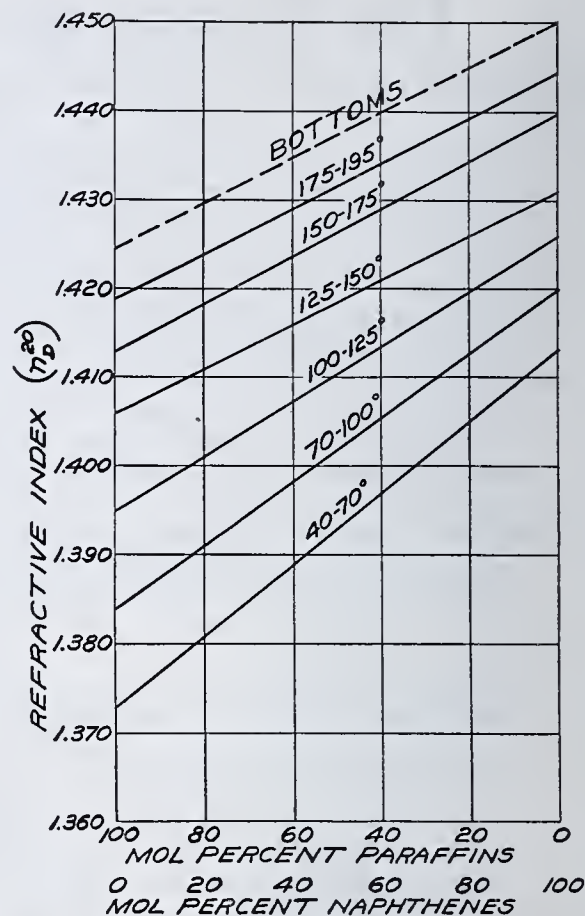


FIGURE 2. REFRACTIVE INDEX-COMPOSITION CURVES FOR PARAFFIN-NAPHTHENE MIXTURES

or sodium sulfate, and determine the refractive index, *n*<sub>D</sub><sup>20</sup>. The proportion of naphthenes present in the mixture is determined from the appropriate curve of Figure 2.

### Errors and Calculations

Mulliken and Wakeman (11) have shown that the bromate bromide method gives accurate results with a large number of aliphatic and cyclic olefins ranging from hexene and cyclohexene to hexadecene and cyclohexylheptene. Check runs made by the authors' procedure (which differs in only minor features from that of Mulliken and Wakeman) on several olefins are summarized in Table I.

TABLE I. BROMINE NUMBER DETERMINATIONS

Substance	<i>B</i> , Calculated	<i>B</i> , Found
20% diisobutylene in iso-octane	29.6	28.2
Cyclohexene	195	188
<i>n</i> -Octenes	143	141
2-Ethyl-hexene-1	143	139
Pentene-1	228	232

Some error is undoubtedly introduced by the presence of diolefins in some cracked gasoline. It is not believed that this error, in general, will be large. If the presence of conjugated diolefins in significant amounts is suspected they may be removed by the procedure of Kurtz and Headington (6) before the distillation of the gasoline.

Absorptions carried out on mixtures of paraffins, naphthenes, olefins, and aromatics of known composition with sulfuric acid of various concentrations showed that the amount of absorption was dependent on both acid concentration and temperature. To eliminate the latter variable 0° C. was chosen as the most conveniently attainable constant temperature; this low temperature has the further advantage of making less violent the absorption with highly olefinic fractions.

At 0° C., with the experimental procedure employed, the acid concentration less than fuming sulfuric containing 2



per cent of sulfur trioxide removed benzene completely from benzene-heptane mixture, as shown in Table II. At the same time, this and more concentrated acids showed absorption of 2 to 3 per cent above the aromatic content.

TABLE II. ABSORPTION OF BENZENE FROM BENZENE-*n*-HEPTANE MIXTURE BY SULFURIC ACID

Expt.	Acid Concentration %	Temperature ° C.	Aromatics		$\Delta n_D^{20}$ <sup>a</sup>
			Present %	Found %	
1	95.6	0	50	5	.....
2	95.6	Room	50	21	.....
3	95.6 <sup>b</sup>	Room	50	46	.....
4	98	0	50	11	.....
5	98	Room	50	50	+0.0062
6	99	Room	50	48	.....
7	100	0	50	29	.....
8	100	Room	50	50	+0.0040
9	Fuming, 5 SO <sub>3</sub>	0	50	50	+0.0032
10	Fuming, 10 SO <sub>3</sub>	0	50	50	+0.0039
11	Fuming, 15 SO <sub>3</sub>	0	50	50	+0.0012
12	Fuming, 20 SO <sub>3</sub>	0	50	53	+0.0002
13	Fuming, 25 SO <sub>3</sub>	0	50	52	+0.0002
14	Fuming, 26.5 SO <sub>3</sub>	-7	50	52	.....
15	Fuming, 26.5 SO <sub>3</sub>	0	50	53	+0.0002
16	100	0	50	32	.....
17 <sup>c</sup>	100	0	26.5	18	.....
18 <sup>d</sup>	100	0	10.4	12.5	.....

<sup>a</sup>  $\Delta n_D^{20}$  = observed index of residue minus index of *n*-heptane (1.3878).

<sup>b</sup> Kattwinkel reagent (30 grams of P<sub>2</sub>O<sub>5</sub> per 100 cc. of acid).

<sup>c</sup> Sample was residue of 16.

<sup>d</sup> Sample was residue of 17.

Lowering of the temperature to -7° C. did not cut down additional absorption. Three successive absorptions with 0 per cent sulfuric acid at 0° C. (experiments 16 to 18) also gave extra absorption, so that this procedure has no advantage over a single extraction with stronger acids.

The results given in Table III show that, although 100 per cent sulfuric acid at room temperature and fuming acid containing 5 to 10 per cent of sulfur trioxide produced the correct absorption from a paraffin-naphthene-olefin-aromatic mixture, no acid weaker than 25 per cent sulfur trioxide leaving sulfuric left a residue of the correct refractive index.

TABLE III. ABSORPTION OF AROMATICS AND OLEFINS FROM A MIXTURE<sup>a</sup>

Expt.	Sulfuric Acid Concentration %	Temperature ° C.	Aromatics + Olefins		$\Delta n_D^{20}$ <sup>b</sup>
			Present %	Found %	
19	95.6 + P <sub>2</sub> O <sub>5</sub> <sup>c</sup>	Room	40	38	.....
20	98	0	40	24	.....
21	98	Room	40	34	.....
22	99	Room	40	36	.....
23	100	0	40	36	.....
24	100	Room	40	40	+0.0081
25	Fuming, 5 SO <sub>3</sub>	0	40	40	+0.0040
26	Fuming, 10 SO <sub>3</sub>	0	40	40	+0.0032
27	Fuming, 15 SO <sub>3</sub>	0	40	43	+0.0019
28	Fuming, 20 SO <sub>3</sub>	0	40	41	+0.0015
29	Fuming, 25 SO <sub>3</sub>	0	40	44	0.0000
30	Fuming, 26.5 SO <sub>3</sub>	-7	40	44	.....
31	Fuming, 26.5 SO <sub>3</sub>	0	40	45	-0.0002

<sup>a</sup> Mixture contained 40 per cent *n*-heptane, 19.5 per cent benzene, 20 per cent cyclohexane, 10.5 per cent octenes, and 10 per cent cyclohexene (volume).

<sup>b</sup>  $\Delta n_D^{20}$  = observed index of residue minus index of 2:1 *n*-heptane:cyclohexane mixture.

<sup>c</sup> Kattwinkel reagent.

In spite of the fact that the latter reagent absorbed 4 per cent more than the total olefin-aromatic content, it was chosen as the best all-round absorbent at 0° C. Methods involving use of weaker acids and distillation to remove polymers were considered undesirable because of the small samples available; furthermore, the results on the benzene-*n*-heptane mixture (Table II), in which polymerization is improbable, make it doubtful whether the 98 per cent sulfuric acid used by Faragher, Morrell, and Levine (3), by Ormondy and Crahan (12), and by others completely absorbs all aromatics.

It is believed that, especially for the lower fractions, the error involved in the estimation of naphthenes and paraffins from Figure 2 does not exceed the experimental error inherent in the other group determinations. The curves were drawn from the average of values reported in the literature for the known hydrocarbons occurring in each fraction. Only those naphthenes likely to occur in petroleum products were considered, however; derivatives of cyclopropane and cyclobutane were excluded. In the higher-boiling naphthene fractions, considerable uncertainty is involved in estimating an average refractive index because of the necessity for including isopropylcyclohexane, the menthanes, and decalin with naphthenes of much lower refractivity. Since the amount of these higher fractions is relatively small in the average gasoline, relatively large errors may be tolerated in the analysis of these fractions without greatly changing the analysis for the entire gasoline. When the C<sub>10</sub> and C<sub>11</sub> fractions are the main constituents of a high-boiling naphtha the authors cannot recommend this method of analysis.

Theoretically, the results should all be expressed in consistent units—i. e., either weight per cent or volume per cent. In practice, however, it has been found more convenient to express the per cent of olefins as the weight per cent experimentally determined; the per cent of aromatics as the difference between the latter quantity and the volume per cent of aromatics plus olefins; and the per cent of naphthenes and paraffins as the mole per cent of the residue left from the sulfuric acid absorption, the amount of residue being expressed in volume per cent.

TABLE IV. CALCULATED RESULTS

Fraction	Weight of Total %	Olefins		Paraffins		Naphthenes		Aromatics	
		A %	B %	A %	B %	A %	B %	A %	B %
Run B6A									
C <sub>5</sub> }	15.1	51	51	6	7	5	4	38	38
C <sub>6</sub> }									
C <sub>7</sub>	28.2	18	18	52	49	8	8	22	25
C <sub>8</sub>	29.0	9	9	56	53	4	3	31	35
C <sub>9</sub>	21.5	3	3	61	56	8	8	28	33
Residue	6.5	30	30	5	5	1	1	64	64
Total gasoline		18	18	45	42	6	6	31	34
Run B6D									
C <sub>5</sub>	0.3	100	100	0	0	0	0	0	0
C <sub>6</sub>	6.1	78	78	4	4	8	8	10	10
C <sub>7</sub>	30.0	16	16	10	9	10	8	64	67
C <sub>8</sub>	21.3	11	11	9	7	8	7	72	75
C <sub>9</sub>	15.2	40	40	1	1	1	1	58	58
C <sub>10</sub>	4.5	71	71	0	0	0	0	29	29
Residue	22.6	52	52	0	0	0	0	48	48
Total gasoline		33	33	5	5	5	5	57	57

The error introduced by mixing units (weight per cent, volume per cent, and mole per cent) becomes smaller the more closely the density of the olefinic portion of each fraction approaches the density of the fraction as a whole, and the percentages approach volume per cents. That this error is well within the experimental error was shown by calculating in two ways the results for two cracked gasolines of widely different composition. The first method of calculation, A, was the convenient one just outlined. The second method, B, expresses all the results as weight per cents, and involves the estimation of average densities for the paraffins and naphthenes of each fraction, conversion of the volume per cent of the paraffin-naphthene mixture to weight per cent, and then finding the weight per cent of aromatics by difference, the olefins being determined as weight per cent experimentally. The results are shown in Table IV.

It should be noted that the deeply cracked gasoline (B6D) shows a jump in olefin content in the fractions boiling above 125° C. (C<sub>9</sub>, C<sub>10</sub>, and residue). The olefins present may be aromatic olefins (styrene and its homologs) since these fractions show unusually high densities and refractive indices. These olefins may therefore be considered either as such or as aromatics, depending upon the purpose of the analysis.



To test the consistency of the entire method, two mixtures were prepared from analyzed cracked gasolines, and the compositions of the mixtures were determined by experiment and found by calculation. A comparison of the results is given in Table V.

TABLE V. COMPARATIVE RESULTS

Sample	Paraffins	Per Cent Naphthenes	Aromatics	Olefins
B17:				
Calculated	69	4	18	9
Found	66	2	23	10
B18:				
Calculated	62	4	21	13
Found	62	3	22	13

In no case do the differences exceed 5 per cent; in most cases they are much lower. It is believed that this value represents also the limit of precision of the method.

### Conclusion

It is clear that the analytical method herein outlined is not rigorously accurate. Nevertheless, in the absence of a simple exact method, the rapidity and simplicity of the operations involved in the procedure, the fact that the errors for different samples tend in the same direction, and the adaptability of the method to the analysis of smaller amounts than

can be used with other procedures, do much to recommend it as a routine method, especially for comparative purposes. As such, it should prove valuable until more exact methods are available.

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## Chemical and X-Ray Diffraction Studies of Calcium Phosphates

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The constancy and purity of composition of various commercial primary, secondary, and tertiary calcium phosphates are estimated. Secondary calcium phosphates are of least variability; primary and tertiary of marked variability.

Evidence of three crystalline forms each of unignited primary and secondary cal-

cium phosphates is found from x-ray studies.

The commercial tertiary calcium phosphates are probably hydroxylapatite with more or less adsorbed phosphate ions resulting in empirical formulas approaching the theoretical value for  $\text{Ca}_3\text{P}_2\text{O}_8$ . Secondary calcium phosphate may be admixed.

DESPITE the profusion of papers on the chemistry of the calcium phosphates, there are many fundamental points still obscure. As Drakunov (11) points out, the study of these important substances involves great experimental difficulties. Larson (20) reported the preparation and properties of primary, secondary, and tertiary calcium phosphates "in pure crystalline form." However, a number of recent investigations offer contradictory evidence especially on the nature of the tertiary calcium phosphates. The work reported herewith proposes to examine the commercially prepared primary, secondary, and tertiary calcium phosphates chemically and by x-ray diffraction studies in order (a) to estimate the constancy and purity of composition of the commercial products, and (b) to interpret the analyses in the light of recent findings on the nature of these compounds. In the interpretations, no attempt will be made to review exhaustively even the recent literature, but only such experiments or hypotheses as seem pertinent will be included.

The commercially prepared calcium phosphates used in this investigation have been obtained from eight different

companies—five in this country, two in Germany, and one in England. Two samples each (of different lot numbers) of the tertiary phosphates and one each of the secondary and primary phosphates were used.

### Analytical Procedure

In each case, samples were taken from the top and bottom of the bottle; inasmuch as no difference was found, these two values served as duplicate determinations on each product. The samples were dried at 105° C., cooled in a desiccator, and analyzed for calcium and phosphorus according to the gravimetric method (accuracy: Ca, 0.3 per cent; P, 1.0 per cent) of Washburn and Shear (28). For ignition, a third sample was similarly dried, cooled, weighed into a platinum crucible, heated for 1 hour at 900° C., cooled, and weighed, and samples were taken for analysis as before.

### X-Ray Diffraction Procedure

For x-ray powder diffraction photographs, an apparatus was used similar in design to the General Electric diffractive apparatus Type YWC, Form D, described by Davey (8). In order to obtain intensity measurements of diffraction maxima, a series of standard densities was obtained by a graduated, accurate



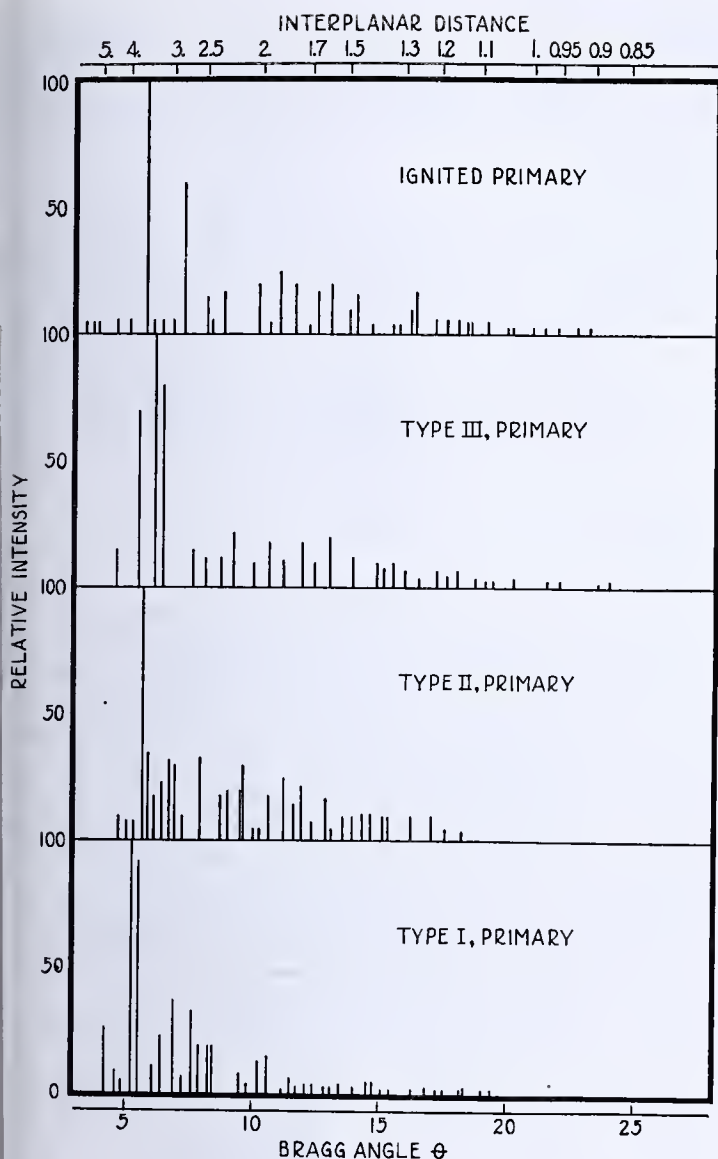


FIGURE 1. X-RAY DIFFRACTION PATTERNS

The "ignited primary" pattern is probably that of calcium metaphosphate. Only this pattern was found after ignition. Before ignition three types of patterns were found which indicate the existence of three crystalline modifications of primary calcium phosphate.

med series of exposures from a constant x-ray source. The film used for the standard was cut from the same sheet on which the diffraction maxima were separately recorded. The standard and the diffraction films were developed together by hand agitation in fresh x-ray developer. Density measurements were made on the diffraction lines, the background adjacent to each line, and the exposure scale. The densitometer utilized an optical slit, a vacuum-type photoelectric cell, and an FP54 electrometer tube with an appropriate electrical circuit.

From these data, the intensities of x-ray diffraction lines and of the adjacent background were calculated in terms of the time required for a standard x-ray beam to produce an equal density. Each chart of an x-ray diffraction diagram has as ordinate the relative intensities of the diffraction maxima over the adjoining background with the intensity of the strongest line set at 100. The abscissas are given both in units of the Bragg angles,  $\theta$ , and the interplanar distance,  $d$ . With hydroxylapatite, powder diffraction measurements were made utilizing both the photographic means and a Bragg-type ionization spectrometer. The resulting relative intensity measurements are similar, indicating that the photographic method gives approximately correct results. Since no correction is made of different amounts of absorption undergone by rays refracted at different angles, only the relative intensities of lines in the same portion of the spectrum may be legitimately compared.

## Primary Calcium Phosphates

In Table I are given the calcium and phosphorus percentages, the percentage weight loss on ignition, and the calcium-phosphorus per cent ratio before and after ignition of the

primary calcium phosphates. The theoretical values for primary calcium phosphate monohydrate and calcium metaphosphate are included for comparison. The calcium values range from 13.5 to 16.6 and phosphorus from 24.2 to 29.9 per cent, the theoretical values for  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  being calcium 15.9 and phosphorus 24.6. Sample E, having a high calcium content and a high calcium-phosphorus per cent ratio, together with a low loss on ignition, may be a mixture containing about 6 per cent of secondary phosphate. All the other samples have calcium percentages less than and phosphorus percentages greater than the theoretical value. The calcium-phosphorus per cent ratios of two samples vary less than 5 per cent from the theoretical; of two others the variation exceeds 15 per cent.

TABLE I. CONSTANCY OF COMPOSITION AND EFFECT OF IGNITION (1 hour at 900° C. on various samples of commercial primary calcium phosphates)

Source	Sample No.	Before Ignition			Loss %	After Ignition		
		Ca %	P %	Ca:P %		Ca %	P %	Ca:P %
A	11	14.6	24.9	0.587	..	18.9	28.3	0.668
B	12	13.5	24.7	0.545	24.8	17.6	30.6	0.575
D	14	15.3	24.8	0.615	..	19.4	30.9	0.628
E	15	16.6	24.2	0.688	20.4	21.0	30.3	0.693
F	16	15.4	24.9	0.616	22.3	19.6	31.3	0.631
G	17	13.8	24.8	0.553	24.7	17.3	30.6	0.566
Theoretical for $\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$		15.9	24.6	0.646	21.4	..	..	..
Theoretical for $\text{CaP}_2\text{O}_6$		..	..	..	..	20.2	31.3	0.646

On ignition, the primary phosphates show percentage losses of 20.4 to 24.8 with an average of 23.1. The theoretical percentage loss for the conversion of the primary monohydrate to calcium metaphosphate is 21.4. The ignited samples were dissolved only after hours of acid hydrolysis, being therefore probably principally calcium metaphosphate. The calcium-phosphorus per cent ratios all show evidence of slight loss of  $\text{P}_2\text{O}_5$  on ignition, a loss possibly explained through the equation of Bassett (2):



In Figure 1 are shown the charts of the x-ray diffraction patterns of primary phosphates before and after ignition. Only one pattern was obtained after ignition from any primary phosphate, regardless of its pattern type before ignition; this "ignited primary" pattern is probably that of calcium metaphosphate. If the ignition product is a mixture of polymers, approximately the same mixture must have occurred in each sample. Hinds (14) stated that calcium metaphosphate is the product of heating primary calcium phosphate, but Larson (20) offers stoichiometric evidence that the product after 170 hours at the temperature of the Meker burner is calcium pyrophosphate. Since the analytical values for the ignited product correspond closely to the theoretical values for  $\text{CaP}_2\text{O}_6$  and since the "ignited primary" diffraction pattern for samples ignited for 1 hour at 900° C. is different from the "ignited secondary" pattern, there seems to be reason under these conditions for agreement with Hind's conclusion.

The three types of primary phosphate patterns before ignition were obtained from samples taken directly from the bottles without drying. In an effort to connect the types of patterns with the water content, samples were heated for periods up to 1224 hours at 105° C. with loss determinations and x-ray diffraction patterns made at 14, 38, 110, 158, 422, and 1224 hours. With the exception of sample E, there was 7.69 to 12.2 per cent loss during the first 14 hours, and less than 2.88 per cent during the next 24 hours, with additional losses ranging from 1.55 to 5.10 per cent up to 1224 hours. Sample E, which probably contained secondary phosphate, showed only 0.69 per cent loss after the first 14 hours and



5.90 per cent after 38 hours with an additional loss of 2.63 per cent up to 1224 hours. Although all the samples gave Type I patterns at the start of the drying and most of them gave Type II and Type III after increasing lengths of time, there was no apparent regularity nor dependence of pattern type on the water content. Sample E, for example, gave only Type II pattern up to 1224 hours; sample B gave Type III after 422 hours and Type II after 1224 hours.

The three types of patterns indicate three crystallographic entities. Only one such pattern has been previously reported (20), a pattern corresponding to Type II. It has been accepted for many years (4) that there are two forms of primary calcium phosphate, the monohydrate and the anhydrous. It would seem that either one may exist in more than one crystalline modification or that there is another hydrate. This third form is unidentified.

### Secondary Calcium Phosphates

In Table II are given the calcium and phosphorus percentages, the calcium-phosphorus per cent ratios before and after ignition, and the percentage weight loss on ignition of the dried secondary calcium phosphates. The theoretical values for anhydrous secondary phosphate and for calcium pyrophosphate are included for comparison.

The calcium values range from 28.5 to 31.4; phosphorus from 21.3 to 22.7 per cent. The theoretical values for

$\text{CaHPO}_4$  are calcium, 29.4, and phosphorus, 22.7 per cent; most of the samples correspond closely to the theoretical values. Sample C has a high calcium, low phosphorus content, and a low loss on ignition; a mixture of approximately 30 per cent  $\text{Ca}_3\text{P}_2\text{O}_8$  and 70 per cent  $\text{CaHPO}_4$  would give the values found.

TABLE II. CONSTANCY OF COMPOSITION AND EFFECT OF IGNITION (1 hour at 900° C. on various samples of commercial dicalcium phosphates)

Source	Sample No.	Before Ignition			Loss %	After Ignition		
		Ca %	P %	Ca:P %		Ca %	P %	Ca:P %
B	22	29.6	22.4	1.32	7.25	32.1	23.0	1.39
C	23	31.4	21.3	1.48	6.30	33.7	22.0	1.53
D	24	28.9	22.7	1.28	8.13	31.9	22.1	1.44
E	25	28.5	22.7	1.26	8.03	31.5	24.0	1.31
F	26	29.3	22.7	1.29	7.62	31.8	23.7	1.34
G	27	29.3	22.5	1.30	8.42	32.1	23.1	1.39
Theoretical for $\text{CaHPO}_4$		29.4	22.8	1.29	6.62	..	..	..
Theoretical for $\text{Ca}_2\text{P}_2\text{O}_7$		..	..	..	..	31.5	24.4	1.29

The percentage weight losses on ignition range from 6.30 to 8.42 with an average of 7.63. The theoretical loss for the conversion  $2\text{CaHPO}_4$  to  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{H}_2\text{O}$  is 6.62. Although the calcium-phosphorus per cent ratios after ignition are uniformly slightly higher than those before ignition, there is no obvious explanation for the loss of  $\text{P}_2\text{O}_5$ . Since the analytical values for the ignition product correspond closely to the theoretical values for  $\text{Ca}_2\text{P}_2\text{O}_7$ , it is probably principally calcium pyrophosphate. Hinds (14) stated that calcium metaphosphate is the final product of heating secondary calcium phosphates, a conclusion probably incorrect for products obtained by igniting for 1 hour at 900° C. The difference between the "ignited primary" and "ignited secondary" diffraction patterns confirms the differences postulated on the basis of analytical results.

In Figure 2 are given the charts of the x-ray diffraction patterns of the secondary calcium phosphates. The "ignited secondary" pattern is probably that of calcium pyrophosphate. Only one pattern was obtained after ignition, regardless of the pattern type before ignition. Several previous reports have included patterns of secondary calcium phosphate. Of the three types of patterns found before ignition (Figure 2), Type III apparently corresponds to the pattern of Larson (20) and of Schleede et al. (24). Type II shows some similarity to the pattern obtained by Schleede on a sample hydrolyzed for 80 hours in warm water. Type I is somewhat like the pattern given by Roseberry et al (23). Of these, only Larson's sample was identified crystallographically; he gave the formula as the "tetrahydrate,"  $\text{Ca}_2\text{H}_7(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , a formula which, lacking further evidence as to the molecular configuration, seems unnecessarily complicated. Only two secondary calcium phosphates have been accepted as unquestioned (4), the dihydrate and the anhydrous. Two others have been described,  $3\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (17, 22) and  $4\text{CaHPO}_4 \cdot \text{H}_2\text{O}$  (10). The three types of patterns found indicate the existence of three crystallographic entities. The findings of Drakunov (11) and Davies (9), that there is no definite temperature at which the dihydrate loses its water, may be some evidence that a lower hydrate is present whose formation is a step in the conversion of the dihydrate to the anhydrous.

### Tertiary Calcium Phosphates

In Table III are given the calcium and phosphorus percentages, the calcium-phosphorus per cent ratios before and after ignition, and the percentage weight loss on ignition of the tertiary calcium phosphates. The theoretical values for  $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$ , hydroxylapatite, and  $\text{Ca}_3\text{P}_2\text{O}_8$  are given for comparison. The calcium percentages found before ignition

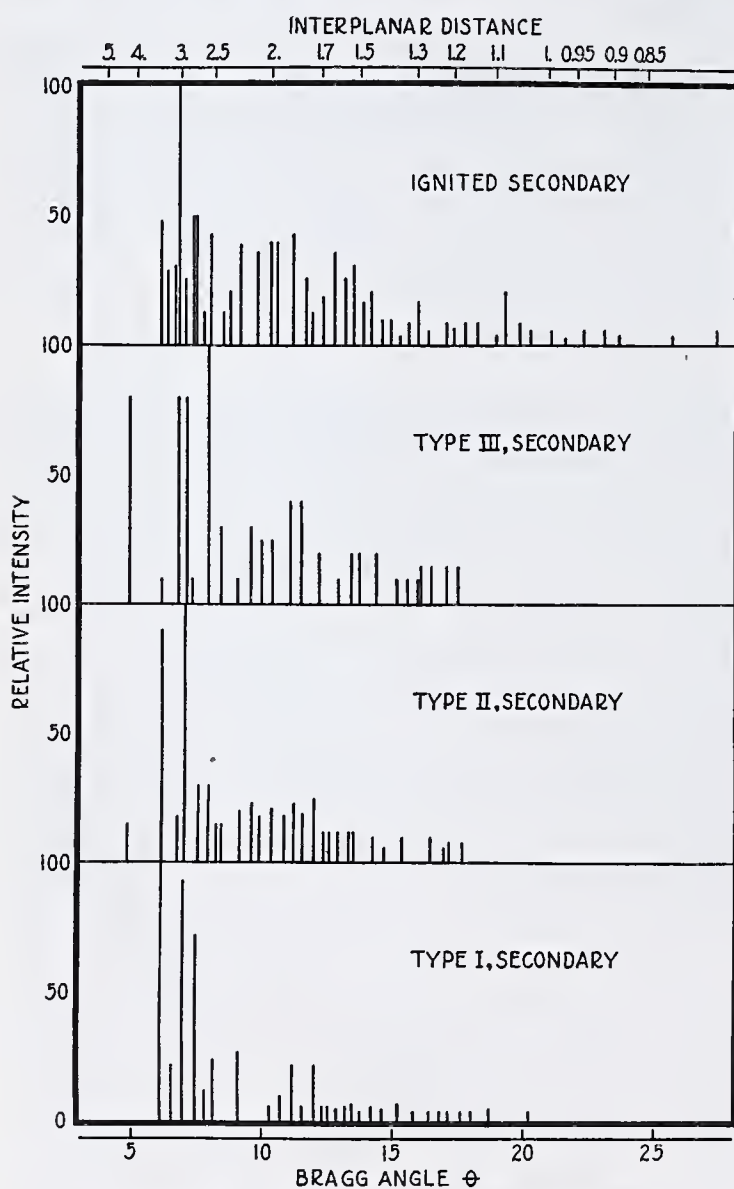


FIGURE 2. X-RAY DIFFRACTION PATTERNS

The "ignited secondary" pattern is probably that of calcium pyrophosphate. Only one pattern is found after ignition. The three types of patterns before ignition indicate the existence of three crystallographic entities.



range from 33.1 to 38.0, the phosphorus from 17.9 to 20.2; the theoretical values for  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  are calcium, 36.6, phosphorus, 18.9 per cent. Comparing the calcium-phosphorus per cent ratios to the theoretical, four samples vary by 0 to 2.5 per cent, five by about 5 per cent, four by about 3 per cent, and two by about 13 per cent (compare 2, 7, 12). The composition of Sample B, *a* and *b*, may be approximated by a mixture of 60 per cent  $\text{Ca}_3(\text{PO}_4)_2$  and 40 per cent  $\text{CaHPO}_4$ ; actually, the x-ray diffraction patterns of these two samples showed lines of both tertiary and secondary calcium phosphates. Such an x-ray finding has been previously reported (23). This mixture has almost exactly the calcium-phosphorus per cent ratio given by Bassett (3) for the intersection of the equilibrium curves of secondary and tertiary phosphates in the system  $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ .

TABLE III. CONSTANCY OF COMPOSITION AND EFFECT OF IGNITION  
1 hour at 900° C. on various commercial samples of tertiary calcium phosphate)

Source	Lot	Sample No.	Before Ignition			Loss %	After Ignition		
			Ca %	P %	Ca:P %		Ca %	P %	Ca:P %
A	<i>a</i>	31	36.0	18.8	1.92	5.27	38.1	19.9	1.92
	<i>b</i>	311	37.9	18.0	2.10	4.72	39.3	18.7	2.10
B	<i>a</i>	32	33.4	20.1	1.67	7.30	36.0	20.7	1.70
	<i>b</i>	322	33.1	20.2	1.69	7.29	35.8	21.5	1.66
C	<i>a</i>	33	36.6	18.3	1.99	4.98	38.8	19.3	2.00
	<i>b</i>	333	37.1	18.3	2.03	6.67	39.0	19.0	2.05
D	<i>a</i>	34	36.8	18.2	2.02	4.88	38.8	19.2	2.01
	<i>b</i>	344	37.4	18.3	2.04	6.10	38.9	18.9	2.06
E	<i>a</i>	35	37.0	18.0	2.05	4.78	38.9	18.9	2.05
	<i>b</i>	355	37.4	17.9	2.09	4.71	38.9	18.8	2.07
F	<i>a</i>	36	36.9	19.0	1.94	4.73	38.8	20.0	1.94
	<i>b</i>	366	38.0	19.3	1.97	1.05	38.4	19.7	1.95
G	<i>a</i>	37	51.5	0.0	..	24.3	..	..	..
	<i>b</i>	377	37.2	18.2	2.04	6.94	38.9	18.9	2.06
H	<i>a</i>	38	35.4	19.7	1.80	5.58	37.7	20.4	1.85
	<i>b</i>	388	35.5	19.6	1.81	5.21	37.6	20.6	1.82
Theoretical for $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$			36.6	18.9	1.94	5.49	..	..	..
Theoretical for hydroxylapatite			39.8	18.5	2.15	..	..	..	..
Theoretical for $\text{Ca}_3\text{P}_2\text{O}_8$			..	..	..	..	38.7	20.0	1.94

The tertiary phosphates show weight losses on ignition ranging from 1.15 to 7.30 per cent with an average of 5.34 per cent. (This does not include the value of 24.3 per cent on sample G, *a*, which was found to be calcium hydroxide.) The theoretical value for the loss of one molecule of water from  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  is 5.49 per cent. Calculating calcium and phosphorus percentages for the ignited product shows that no loss of either occurs, a fact borne out by the experimentally found identity of calcium-phosphorus per cent ratios before and after ignition.

The charts of the x-ray diffraction patterns of the tertiary calcium phosphates before and after ignition are shown in figure 3. The patterns of the various samples before ignition were either that of an apatitelike substance or of a superimposing of this pattern on that of  $\text{CaHPO}_4$ . Only one new pattern is found after ignition; this pattern corresponds to that called the  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$  pattern (16). The various samples after ignition gave either the  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$ , the original hydroxylapatite pattern, or the two superimposed. After ignition the samples containing  $\text{CaHPO}_4$  there were no lines evident of the "ignited secondary" pattern, a fact which may be tentatively attributed to a reaction between hydroxylapatite and secondary calcium phosphate at high temperatures as follows:



Thus, only the pattern of  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$  was obtained from sample B, *a* and *b*, after ignition (compare Tables III and IV). On the basis of the diffraction patterns and the chemical data, it is possible to give a fairly coherent description of the tertiary phosphates. It should be emphasized that

TABLE IV. COMMERCIAL TRICALCIUM PHOSPHATES  
(Correlation of Ca:P per cent ratios and x-ray diffraction patterns after ignition)

Sample	Ca:P %	Remarks
311	2.10	Predominantly hydroxylapatite pattern after ignition
355	2.07	
344	2.06	
377	2.06	
35	2.05	Predominantly $\beta\text{-Ca}_3\text{P}_2\text{O}_8$ pattern after ignition
333	2.05	
34	2.01	
33	2.00	
366	1.95	
36	1.94	Only $\beta\text{-Ca}_3\text{P}_2\text{O}_8$ pattern after ignition
31	1.92	
388	1.82	
32	1.70	
322	1.66	

although the particle size is extremely minute the precipitated tertiary phosphate is crystalline.

From phase-rule and other studies (2, 5, 6, 10, 13, 15, 19, 20, 23-27, 29) two principles may be laid down: If the precipitated phosphate has a composition approximating  $\text{Ca}_3\text{P}_2\text{O}_8$ , the ignited product gives the pattern called  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$ ; and if the composition approximates hydroxylapatite, the lattice is heat-stable at 900° C. This interpretation is shown to be valid by the comparison of the diffraction patterns of the ignited commercial tertiary phosphates and their respective calcium-phosphorus per cent ratios (Table IV). Four samples whose calcium-phosphorus per cent ratios average 2.07 give predominantly hydroxylapatite patterns after ignition; five samples whose calcium-phosphorus per cent ratios average 2.01 show small amounts of hydroxylapatite but predominant amounts of  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$ ; five samples whose calcium-phosphorus per cent ratios average 1.81 show only the  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$  pattern after ignition.

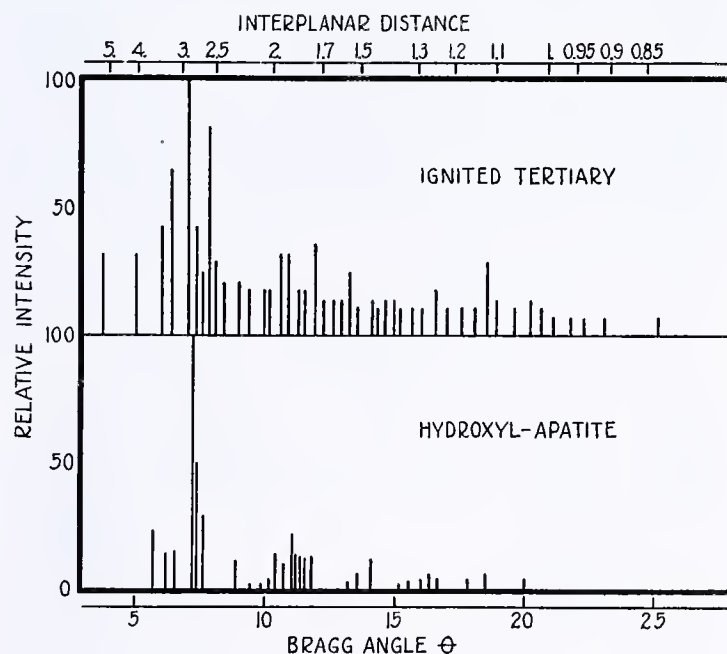


FIGURE 3. X-RAY DIFFRACTION PATTERNS

The "ignited tertiary" pattern is that of  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$  (15). After ignition the commercial tertiary calcium phosphates gave either this pattern only or this pattern superimposed on the hydroxylapatite pattern. The hydroxylapatite pattern was obtained from all the tertiary phosphates before ignition. In certain samples the pattern of secondary calcium phosphate was also present.

In an attempt to obtain some light on the mechanism of the precipitation and the nature of the precipitated "tertiary" calcium phosphates, the mode of precipitation was studied in relation to the composition of the precipitate. In a paper which must be considered as preliminary, this approach was offered by Trömel and Möller (27). From the method for



TABLE V. EFFECT OF MODE OF PRECIPITATION AND AMOUNTS OF Ca AND PO<sub>4</sub> ON CHEMICAL COMPOSITION OF PRECIPITATES

Sample	Before Ignition			Loss 900° C.	After Ignition			Sample	Before Ignition			Loss 900° C.	After Ignition		
	Ca %	P %	Ca:P %		Ca %	P %	Ca:P %		Ca %	P %	Ca:P %				
A. Theoretical Amounts of Ca and PO <sub>4</sub> Used to Prepare Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> , Ca Added to PO <sub>4</sub>								C. Theoretical Amounts of Ca and PO <sub>4</sub> Used to Prepare Hydroxylapatite, PO <sub>4</sub> Added to Ca							
T1	35.9	18.7	1.92	3.46	37.8	19.7	1.92	H1	38.4	18.3	2.10	..	39.7	18.9	2.10
T2	36.1	18.6	1.94	3.25	38.0	19.6	1.94	H2	38.4	18.2	2.11	2.41	39.8	18.8	2.12
T3	36.1	18.7	1.93	3.36	37.7	19.5	1.93	H3	38.4	18.2	2.11	2.75	39.8	18.7	2.13
T4	35.8	18.6	1.92	3.39	37.5	19.4	1.93	H4	38.0	18.4	2.07	3.10	39.5	19.0	2.08
T5	36.7	18.6	1.97	3.09	37.6	19.4	1.94	H5	38.2	18.2	2.10	2.96	39.6	18.8	2.11
B. Theoretical Amounts of Ca and PO <sub>4</sub> Used to Prepare Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> , PO <sub>4</sub> Added to Ca								H6	38.0	18.3	2.08	3.10	39.6	18.9	2.10
TR1	38.2	18.1	2.11	3.52	39.9	18.8	2.12	D. Theoretical Amounts of Ca and PO <sub>4</sub> Used to Prepare Hydroxylapatite, Ca Added to PO <sub>4</sub>							
TR2	37.4	18.4	2.03	4.48	39.3	19.2	2.05	HR1	36.8	18.7	1.97	3.78	38.4	19.6	1.96
TR3	38.3	17.9	2.14	2.95	39.4	17.6	2.24	HR2	36.9	18.7	1.97	3.35	38.4	19.4	1.98
TR4	38.0	18.0	2.11	3.50	39.8	18.7	2.13	HR3	37.0	18.7	1.98	3.50	38.2	19.5	1.96
TR5	38.1	18.0	2.12	3.62	39.3	18.9	2.08	HR4	37.1	18.7	1.98	3.68	38.4	19.5	1.97
TR6	38.4	18.1	2.12	2.87	39.6	18.7	2.12	HR5	37.1	18.6	1.99	3.46	38.9	19.4	2.01
								HR6	37.4	18.7	2.00	..	38.4	19.4	1.98

preparing "pure, crystalline" tertiary calcium phosphate described by Larson (20), conditions were established for precipitation.

Four sets of preparations were obtained by (a) following Larson's procedure in which calcium chloride solution was added dropwise to Na<sub>2</sub>HPO<sub>4</sub> solution in calculated amounts to give Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, (b) adding the phosphate to the calcium solution, and (c) and (d) repeating (a) and (b) using amounts of calcium and phosphate to give hydroxylapatite instead of tricalcium phosphate. The analytical data are given in Table V for the precipitates before and after ignition. It is evident from part A that precipitates may be prepared having the theoretical calcium-phosphorus per cent ratio of tricalcium phosphate with far less variation than is found in the commercial samples. Furthermore, the composition of the precipitated phosphates is seen to depend upon the mode of precipitation rather than on the amount of reactants (in the ranges used).

When the diffraction data are correlated with the analytical data (Table VI), it seems evident that the stable precipitated phase, under the conditions described, has the hydroxylapatite lattice. In those precipitates having a calcium-phosphorus per cent ratio less than the theoretical value for hydroxylapatite, apparently the excess phosphate may, on ignition, react with the hydroxylapatite to produce Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub> in amounts limited by the amount of excess phosphate (18).

TABLE VI. EFFECT OF MODE OF PRECIPITATION AND AMOUNTS OF Ca AND PO<sub>4</sub>

(On the chemical composition and crystal lattice of precipitates before and after ignition)

Mode of Precipitation	Theoretical Amounts of Ca and PO <sub>4</sub> to Give	Average Ca:P% Ratio		X-Ray Diffraction Pattern	
		Before ignition	After ignition	Before ignition	After ignition
Ca → PO <sub>4</sub>	Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub>	1.93	1.93	Hydroxylapatite	β-Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub>
PO <sub>4</sub> → Ca	Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub>	2.12 <sup>a</sup>	2.12	Hydroxylapatite	Hydroxylapatite
PO <sub>4</sub> → Ca	Hydroxylapatite	2.10	2.10	Hydroxylapatite	Hydroxylapatite
Ca → PO <sub>4</sub>	Hydroxylapatite	1.98	1.98	Hydroxylapatite	Predominantly β-Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub>

<sup>a</sup> One precipitate having a Ca:P% ratio of 2.03 is not included.

A tentative mechanism for these precipitations may be derived if the precipitates are considered as coacervates (16). The phosphate ions being multipolar do not rapidly lose their water shell and assume, with the calcium and hydroxyl ions, the complicated space orientation of the apatite unit cell. Evidence to this effect may be found (1) in the extremely minute crystals always obtained (10<sup>-6</sup> cm. in length, approximately, 1) and (2) from the high water content of the precipitates—e. g., one precipitate which weighed 2 grams contained 0.2 gram of dry (100° C.) phosphate or approximately 1000 per cent of water. This water is partly lost at 100° C. but some is so tightly bound that successive amounts are re-

moved by heating for long periods at 300°, then 500° and then even at 750° C. (20). (3) On ignition of heat-stable hydroxylapatite precipitates, there is always a marked sharpening of the diffraction lines, indicating the increase of crystal size due to the addition of the less perfectly orientated atoms to the apatite lattice (21).

During precipitation, if the solution is rich in phosphate (Table VI, 1 and 4), many multipolar phosphate ions are drawn around the tiny crystals, attach themselves weakly with only a partial loss of their attractive forces for the water shell, and constitute, together with the crystal, coacervated particles. This precipitate will consequently contain an excess of phosphate, the calcium-phosphorus per cent ratio will be less than the theoretical for hydroxylapatite, and, upon ignition, there may be a reaction between the excess phosphate and the crystal of hydroxylapatite producing the β-Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub> lattice in amounts limited only by the amount of excess phosphate. Thus, depending on the calcium-phosphorus per cent ratio of the ignited precipitate, the pattern may be hydroxylapatite, intermixtures of hydroxylapatite and β-Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub>, or β-Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub>. This hypothetical mechanism is similar in many respects to that offered by Trömel and Möller (27) on the basis of their preliminary work.

Summary

Commercial primary and tertiary calcium phosphates vary considerably from the theoretical composition. Secondary calcium phosphates are of greater constancy of composition and vary little from the theoretical values.

Primary and secondary calcium phosphates each exist in three crystallographic modifications. In each case, one form may be a hydrate, another the anhydrous, while the third is unidentified.

Regardless of the crystallographic form of the primary calcium phosphate, there is only one crystal form after ignition, probably calcium metaphosphate. Regardless of the crystallographic form of the secondary calcium phosphate before ignition, there is only one crystal form after ignition, probably calcium pyrophosphate.

Commercial tertiary calcium phosphates are probably hydroxylapatite with more or less adsorbed phosphate ions to give empirical formulas approaching the theoretical. On ignition at 900° C. for 1 hour, a reaction between the hydroxylapatite and the adsorbed phosphate ions takes place which produces β-Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub>, the amount of change depending on the amount of adsorbed phosphate ions.

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# Analysis of Caustic Liquors for Traces of Impurities

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THE technic for the spectrochemical analysis of caustic liquors for small traces of aluminum, calcium, chromium, copper, iron, lead, magnesium, manganese, silicon, and strontium has been worked out at the Physics Laboratory of the University of Michigan for The Mathieson Alkali Works, Inc., under the auspices of the Department of Engineering Research.

It became important in the alkali industry to be able to determine correctly the amounts of certain elements present in caustic liquors, especially the caustic materials supplied to the rayon industry. Some of the elements cannot be determined very precisely by chemical methods in the range of abundance in which they occur in caustic liquors. The problem was undertaken because the development of spectroscopic methods had reached the point where it seemed possible to obtain the necessary precision in this manner. In addition, saving of time is an important item and is enhanced because spectroscopic analyses for all the elements can be carried out in one operation.

The problem was not a simple one. The material to be analyzed was caustic liquor, a solution of sodium hydroxide,

which could be controlled as to strength; but, no matter what the concentration of the solution, the ratio of the impurities to the sodium hydroxide was extremely small. Since sodium is ionized and excited very easily, it was a problem to find a type of source in which the impurities would be sufficiently excited in the presence of the overwhelming abundance of sodium to permit accurate measurements on their lines. The source had to possess all the characteristics of constancy and sensitivity required for precise analytical work.

The method employed has been previously described (2). It is a method of internal control (3) in which the analysis is made from measurements on the relative intensities of spectral lines of the test elements and of a control element which is present in or is introduced into the specimen in a definite and constant amount. The relative intensity of such a pair of lines is therefore a function of the abundance of the test element, and this function must be determined for each element. By measuring the relative intensities of a selected pair of lines excited in a suitable spectroscopic source for a series of prepared solutions in which the amount of the test element is varied over the range desired, the required function can be discovered. The function is usually expressed as a relationship between the logarithm of the relative intensities of a selected line of the test element and of the control element and the logarithm of the percentage abundance of the test element. The graph of this function is used as the working basis for the determination of that element. Those lines are used ordinarily which give a linear function when plotted as described; a typical working curve is shown in Figure 1.

The relative intensities of the spectral lines are measured by well-proved methods of spectral photometry (4). The technic has been developed to such a degree of reliability that repeat measurements on a single plate agree within  $\pm 1$  per cent and on different plates usually within  $\pm 3$  per cent. The principal problem, therefore, in the development of a technic for spectrochemical analysis lies in the discovery or development of a suitable spectroscopic source of sufficient constancy.

## Development of Source

After trying several sources suggested by previous experience, the high-voltage alternating current arc (1) was found the most suitable. This consists of an arc between two electrodes of carbon of the highest purity, upon each of which a drop of the test solution has been dried.

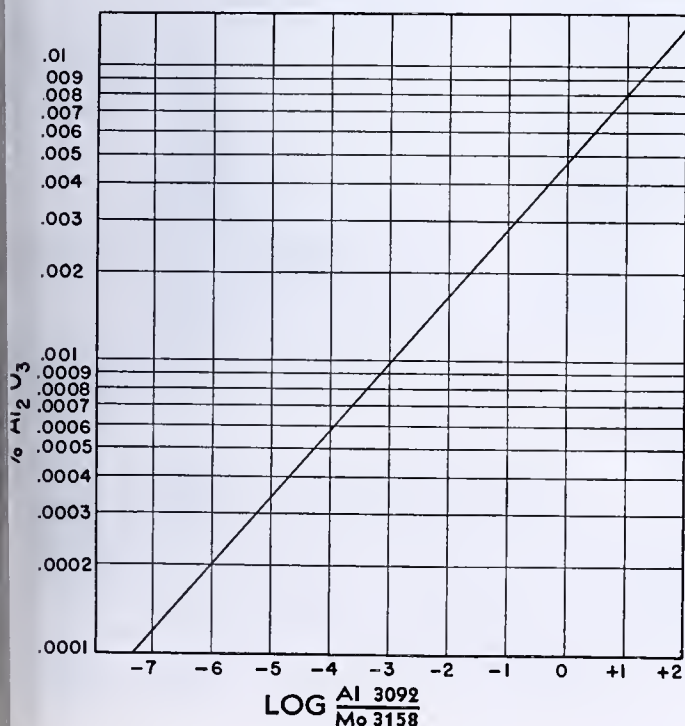


FIGURE 1. TYPICAL WORKING CURVE



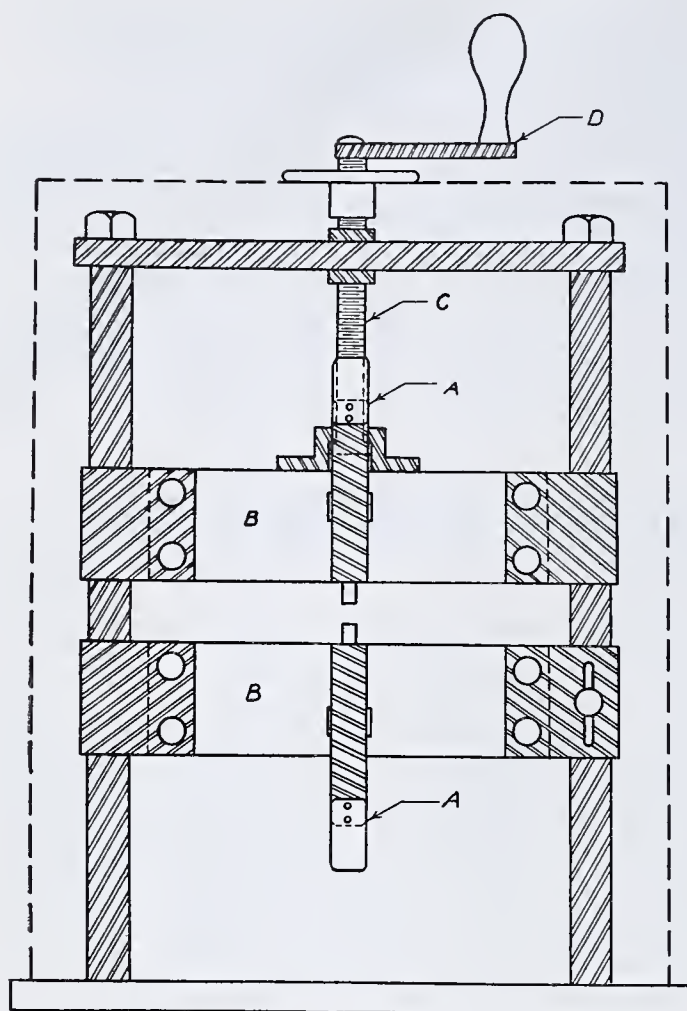


FIGURE 2. ARC STAND

The arc stand is shown in Figure 2. *A, A* are spring clips for holding the carbon electrodes; *B, B* are Bakelite insulators; and *C* is a screw of 0.5-mm. pitch which may be turned by an insulated handle, *D*. The lower electrode is adjusted in position by sliding it on the uprights, and the upper electrode is set by means of the screw. As the arc is operated in a 2200-volt circuit of considerable power, the operator must be guarded against dangerous shock. For this reason, the arc stand is enclosed in a protecting cage with an automatic switch on the door, so that the circuit is broken when the door is opened. The only part of the arc stand protruding through the cage is the insulated handle for adjusting the position of the upper electrode.

The electrodes of the arc are made from the highest grade of spectroscopic carbons. They are carefully cut at right angles to their length, so that the ends are perfectly flat and smooth, and the edges are rounded off slightly with a clean file in order to keep the arc from striking the sharp edges of the electrodes.

After the carbons have been prepared, a drop of the sample to be analyzed is placed on one end of each carbon. A glass rod is dipped into the solution, properly adjusted as to concentration and containing the internal standard, and the ends of the carbons are touched with the droplet on the end of the rod. Sufficient liquid is thus transferred to cover the end of the carbon, the exact amount not being important. The solution is dried by any convenient method, leaving the ends of the

carbons covered with a thin film of solid material. The entire end must be covered, leaving no bare spots where the carbon is exposed, so that the arc plays at all times upon the test material and not upon the carbon. A Pyrex glass rod must be used for caustic liquors, as the sodium hydroxide dissolves soft glass sufficiently to affect the analyses for lead, silicon, and calcium.

The electrodes thus prepared are placed in position in the spring clamps of the arc stand, but are not allowed to touch, so that the solid material is not disturbed. With the required voltage applied to the arc gap, the electrodes are brought close enough together for the arc to strike. After 30 seconds of operation, the circuit is opened and the gap is set at 0.5 mm. by bringing the electrodes into contact and then reversing the screw one full turn. The arc is now ready for record exposures.

The arc is excited by an ordinary 5-kilowatt 60-cycle pole transformer, wired to produce 2200 volts at the secondary terminals. Sufficient resistance is introduced in series with the arc in the secondary circuit to limit the arc current to 2.5 amperes. For this purpose a bank of ordinary cone-type electric heater units has been found convenient. A sufficient number of these are used in combination so that they are not strongly heated by the arc current and the resistance remains constant. This is important because it is necessary to maintain a constant current during the exposure. As the resistors are in the high-voltage secondary circuit, it is wise to mount them in a protecting cage as is shown in Figure 3, in which the entire apparatus is pictured.

The effect of a variation in the arc current on the relative intensities of the spectral lines is shown graphically in Figure 4; the importance of maintaining a constant current is at once apparent. In practice, a current fluctuation of more than  $\pm 0.05$  ampere will introduce errors greater than is generally desirable; therefore the primary current supply should be steady. The service lines should have sufficient capacity so that normal variations of the load on the line will not cause sharp fluctuations of the current.

The arc gap must always be set at the same value when exposures are made, because the conditions of excitation of the spectra and the relative intensities of the spectral lines vary with the arc length, as shown by Figure 5. Because the log ratios of intensities of a number of lines with respect to those of the internal control have a maximum for an arc gap of 0.5 mm., this width was chosen as the standard.

### Determination of Working Curves

Working curves for the analyses were determined from measurements on prepared solutions in which each test ele-

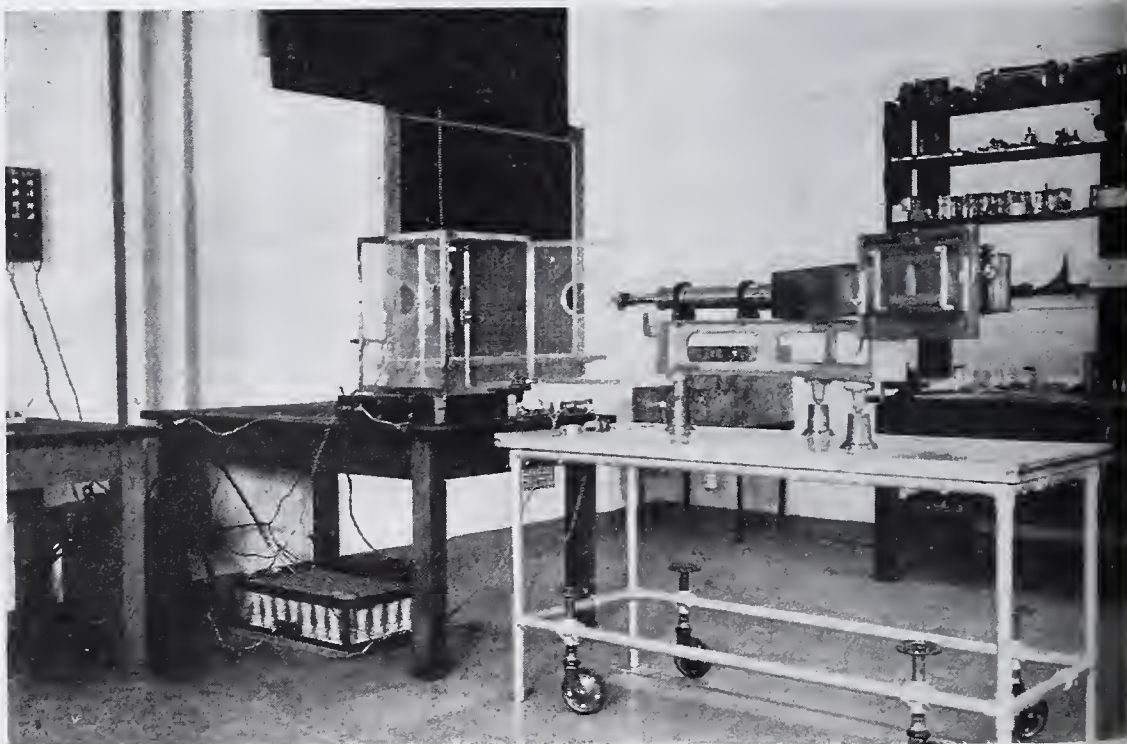


FIGURE 3. SPECTROSCOPIC ARRANGEMENT



ment in turn was varied in percentage abundance. A single internal standard, molybdenum, introduced into the test sample as sodium molybdate, sufficed for all the elements. One cubic centimeter of sodium molybdate solution containing 2 per cent of molybdenum was added to 100 cc. of 25 per cent sodium hydroxide solution. The molybdenum furnished spectral lines near enough to those of the test elements to serve as the internal control for all, and the lines selected were of such intensity that analyses could be made for all the test elements from a single exposure. The only exception was calcium, for which a separate exposure had to be made.

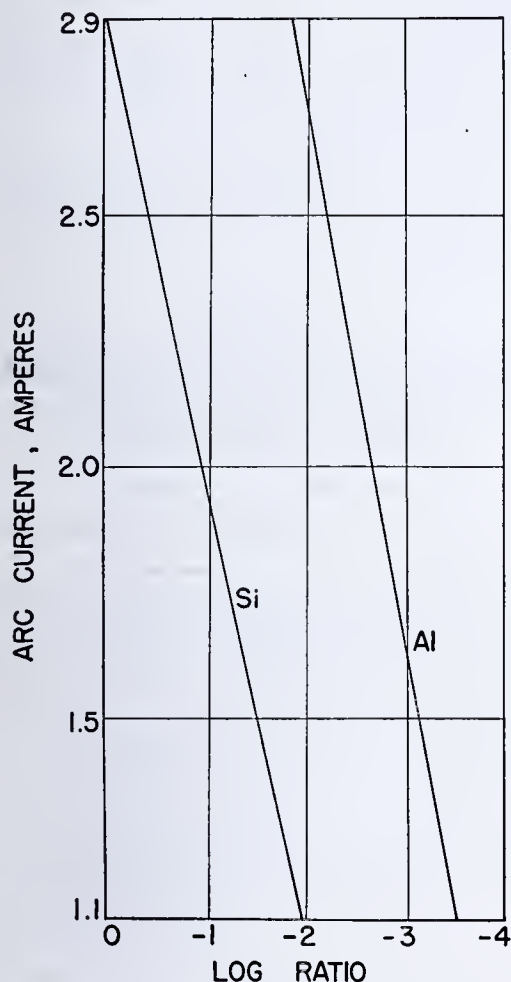


FIGURE 4. EFFECT OF VARIATION IN ARC CURRENT

The exposures are made ordinarily without a condensing lens between the source and the slit of the spectrograph. When very pure caustic liquor was analyzed, however, so long a time was required to photograph the lines to a sufficient density for accurate measurement that the material in the carbons was depleted. To shorten the exposures for such cases a condensing lens was used, so placed that the convergent beam formed by it had a cross section of about 1 cm. at the slit of the spectrograph, and an image of the arc was formed at the collimator lens. It was found best not to form an image of the arc on the slit, because such an image forms an erratic source on account of flickering as the arc wanders.

The determination of the working curves presented a most interesting problem. In some specimens of caustic liquor, impurities are present in extremely minute quantities; no purer solutions could be prepared, even from the best materials obtainable. In order to extend the range of analysis to include these very pure specimens, it was necessary to make allowance for the presence of several elements in the prepared solutions used in determining the working curves.

A method for estimating the amount of a given element present in the stock solution had to be discovered. When the log ratio of the intensities of the selected lines was plotted against the log percentage abundance of the test element for a series of prepared solutions in which the amount of the test element varied systematically, the graph, instead of being a straight line as is to be expected (Figure 1), was curved in the range of the lowest concentrations of the test element.

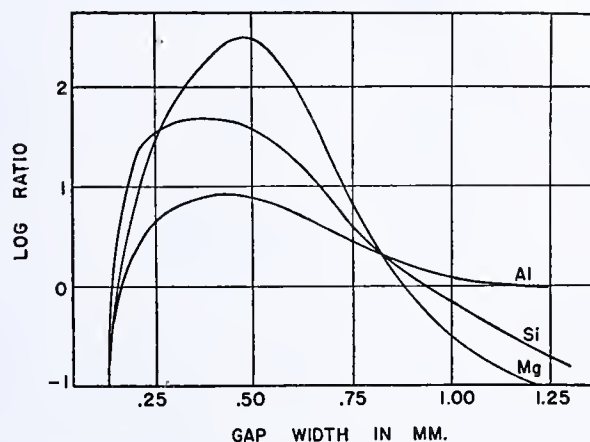


FIGURE 5

The departure from a straight line was in the direction expected if the materials from which the solutions were prepared contained a trace of the test element as an impurity.

A specimen graph is given in Figure 6. The fact that the graph becomes straight for larger amounts of the test element indicates that the amount present as an impurity in the materials is small compared with the amount added to make up the prepared solutions, and becomes negligible in ratio to the added amounts in the range of the larger per-

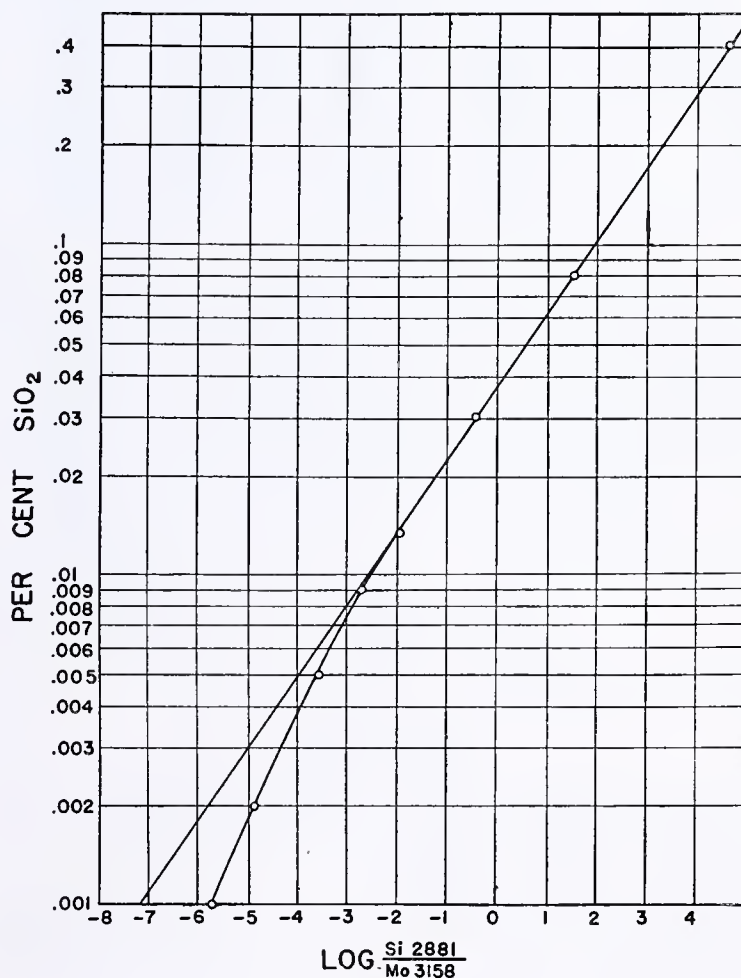


FIGURE 6



centage abundance where the line is straight. If now the straight portion is extended through the smaller percentage range, the amount of the departure of the curve from the straight line gives a measure of the amount of the element present in the original materials. Thus, a correction can be made for residual impurities and applied throughout the range of the working curves. This procedure was followed in determining the working curves for all the test elements.

TABLE I. COMPARATIVE RESULTS

Impurity	Spectrographic %	Chemical I %	Chemical II %
SiO <sub>2</sub>	0.050	0.053	0.054
Fe <sub>2</sub> O <sub>3</sub>	0.0004	0.0005	0.0003
Al <sub>2</sub> O <sub>3</sub>	0.0106	0.0050	0.012
CaO	0.0011	0.0020	0.0003
MgO	0.00058	0.0015	0.0005
Ni	0.00004	0.000044	None
Cu	0.000155	0.00010	
Mn	0.000054	0.00005	
Cr	No trace	Less than 0.000002	

The method of analysis described above has been repeatedly tested for uniformity and accuracy of results. Repeat analyses of the same specimen show a deviation from the mean of not more than 5 per cent of the amount present—within the deviation that might be caused by errors in measuring the densities of the spectral lines on the photographic plate and by the nonuniformity of the plate. Check analyses of different specimens were made by chemical methods. In Table I the results of the spectrographic method are compared with those of two independent chemical analyses made by analysts in different laboratories. The widest variations are for those elements which are most difficult to determine by chemical methods.

TABLE II. SPECTROGRAPHIC ANALYSIS

Impurity	Spectral Lines		Range of Analysis,	
	Impurity Å.	Mo Å.	25% Caustic Liquid %	%
Al as Al <sub>2</sub> O <sub>3</sub>	3092	3158	0.0001	— 0.014
Ca as CaO	4226	3903	0.000054	— 0.005
Mg as MgO	2795	2816	0.00005	— 0.036
Si as SiO <sub>2</sub>	2881	3158	0.001	— 0.10
Cr	2835	3158	0.00002	— 0.010
Cu	3247	3158	0.000010	— 0.005
Fe	3020	3158	0.00001	— 0.010
Mn	2798	2816	0.000002	— 0.00052
Ni	3414	3158	0.000075	— 0.010
Pb	2833	2816	0.00002	— 0.0034
Sr	4077	3903	0.00001	— 0.010

The spectral lines used for the determination of the several elements, those of the control element, and the ranges of percentage abundance for which working curves have been plotted are given in Table II. Experiments indicate that it should be possible by modifications of the spectroscopic source to extend the ranges of analysis to still lower values, as well as to high values. The spectrograph employed was a quartz instrument of medium dispersion giving a spectrum 20 cm. (8 inches) long for the range 7500 to 2100 Å. Eastman polychrome plates were used. A metal step diaphragm (4) was used for producing the calibration patterns on the plates and a clear glass gas-filled 250-watt tungsten lamp was found satisfactory as continuous source for the production of these patterns.

### Applications

The method described for caustic liquors has been used successfully for determining traces of impurities—nickel and chromium plating solutions, various inorganic and pharmaceutical chemicals, and plastics. Urine and saliva have been analyzed for sodium, potassium, calcium, and magnesium by a similar procedure (2), and the technic has recently been perfected for determining lead in urine, beverages, and other liquids, as well as organic tissues. Lead can be de-

termined in this way when present in amounts down to 0.1 mg. per liter. The same spectroscopic source has been successfully applied in the analysis of steels and other metallic alloys. Glass, carbon, and graphite products have been analyzed for metallic elements by modifications of this method, using the type of source described. Experience indicates that this source and general procedure are capable of extremely wide application.

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RECEIVED December 7, 1937. Presented before the Division of Physical and Inorganic Chemistry, Symposium on Quantitative Spectrographic Analysis, at the 94th Meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937.

## Melting Point Determinations under Mercury

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THE relative inertness and high density of liquid mercury have been ingeniously employed to determine the melting points of resins and waxes (2). The solid is fixed below the surface of the mercury either by melting the material and then allowing it to solidify on the walls of a glass tube or by packing the finely ground solid into a capillary; heat is applied and the temperature at which the material rises to the surface of the mercury or the mercury falls through the bottom of an open tube is noted. Since many resins are thermo-reactive, premelting of the resins may change their melting points (1). The operation of stuffing such materials as soft waxes into capillary tubes may become tedious. Moreover, these methods do not seem to take full advantage of the fairly high thermal conductivity of mercury.

The method proposed here consists essentially of affixing a small piece of the original solid to the bulb of a thermometer by means of a piece of wire. The thermometer bulb is then

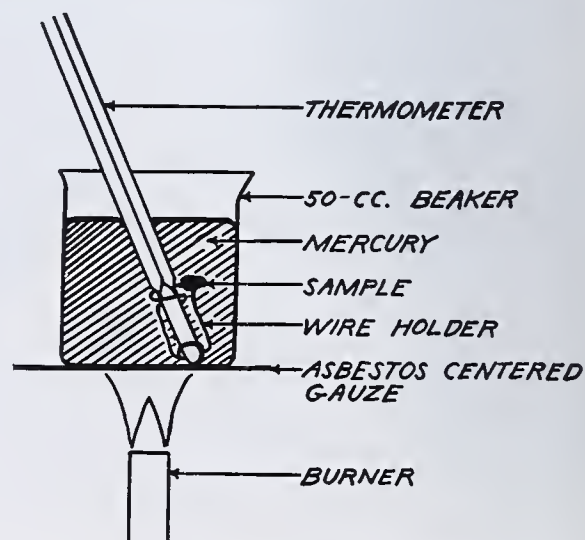


FIGURE 1. ARRANGEMENT FOR MELTING POINT DETERMINATION



submerged in a relatively large volume of mercury contained in a small beaker, so that the solid is completely surrounded by mercury except where it is held by the wire. The beaker is heated directly, so that the mercury serves as the bath medium. A good sample size is about 0.1 cc. The wire holder should be of a material not forming an amalgam. The heating rate should be approximately 5° C. per minute. A suitable arrangement is indicated in Figure 1.

Since there is a rather large exposed surface of hot mercury, it is essential that the work be carried out under a hood or that other means be provided for protection against the mercury vapor.

Satisfactory results have been obtained for a number of substances, including carnauba wax, candelilla wax, Glyco Wax A, and benzoic acid. The method requires very small samples, is rapid, and is practically foolproof.

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## Photoelectric Relay Unit

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FOR some time it has been known that liquids of sufficient opacity reduce the current in a photoelectric cell when cutting off the light entering the cell, and dyes, suspended materials, or small floats have been added to trans-

With suitable slits on both sides of the container in line with the photoelectric cell and light source, a passing meniscus would cut off the light entirely, reduce the photoelectric current and cause the operation of the relay.

After the meniscus has passed, the relay may return to its original setting. Although the current in the photoelectric cell may be different with liquid in place of air in the light beam, the relay circuit can be regulated with liquid in the beam beforehand by adjusting the potentiometer provided with the unit.

In Figure 2, the light beam passing through the empty part of the cylinder keeps the relay circuit open to the buzzer. When the meniscus interrupts this beam, the buzzer sounds, and stops sounding when it has passed.

A water meniscus rising in a 100-ml. graduated cylinder operated the buzzer when passing the beam from a 50-watt lamp with the potentiometer set at 233°.

Meniscus action on a light beam to a photoelectric cell is used in a new device (U. S. Patent 1,953,716, the Distillograph) to record distillation data automatically. The volume of distillate is recorded by means of a photoelectric cell operated by the meniscus as it rises in the receiver, and at the

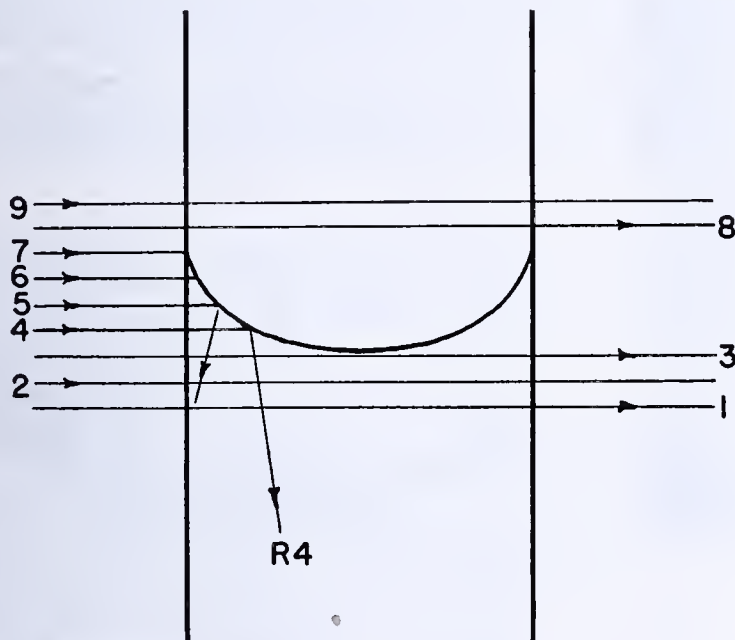


FIGURE 1

parent liquids to reduce the light to the 'electric eye.' However, a meniscus acts like an opaque plate in a liquid column for a limited distance. This limited distance of opacity is at that point in the curvature of the liquid surface where total reflection takes place when light strikes at an angle exceeding the critical angle. It can be made to cut off the light passed through a slit 0.5 cm. wide and 2 cm. long.

In Figure 1 rays of light 4 and 5 would fail to get through the liquid meniscus if their angles of incidence exceeded the angle of total reflection of the liquid in the container. Rays 6 and 7 would be modified in direction.

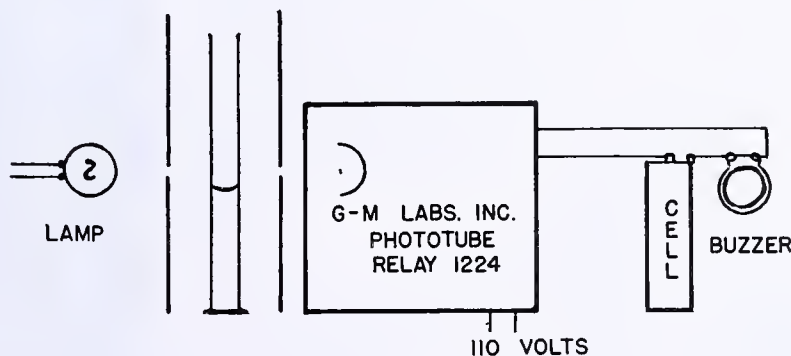


FIGURE 2

same time temperatures from the stillhead are graphed at the volumes desired.

RECEIVED January 4, 1938.



# Melting Point Studies of Binary and Trinary Mixtures of Commercial Waxes

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MELTING points of waxes or of wax mixtures vary somewhat, depending upon the method used for the determination. The true melting point methods, although they cover a wide range of manipulative art, do not differ widely in principle. They are based on two general principles: observation of the temperature at which the opaque wax becomes transparent, or observation of the temperature at which the wax ceases to adhere to an object to which it has

Twelve aluminum pellets are fastened to the plate by means of the waxes to be studied. These pellets are small cylinders 5 mm. in diameter and 6 mm. long. They are slightly convex on one end, so that they will readily drop from the plate as soon as the wax becomes molten.

In making a series of melting point determinations with this apparatus, the wax mixtures are prepared on a large spot plate, which is placed on a water bath until all samples are molten. The brass melting point plate, together with the required number of aluminum pellets, is placed on an adjacent water bath, and heated simultaneously with the spot plate. When the wax samples are completely melted, each pellet is transferred with a forceps from the brass plate to one of the depressions in the spot plate, care being taken that the convex side of each pellet is towards the bottom. When all the pellets have been transferred to the spot plate, the brass plate is placed horizontally on a ring clamped about 7.5 cm. (3 inches) above the spot plate. This keeps the plate at just the right temperature to prevent too rapid cooling of the wax, but at the same time ensures its solidification in a practical length of time.

The pellets with an adhering drop of wax mixture are now transferred from the spot plate to their positions beneath the corresponding numbers on the brass plate (Figure 2). Time for cooling should be allowed before the adjacent pellet is put in place. When all the pellets are in place, the plate is allowed to cool for a few minutes, and then is transferred to the beaker containing the water and thermometer for the melting point determination (Figure 1).

The actual determination of the melting points of the waxes used in fastening the pellets to the brass plate is made by recording the temperature at which the individual pellets drop from the brass plate.



FIGURE 1. APPARATUS

been attached by melting and cooling. In addition to these types of methods, too numerous to refer to specifically and differing in the results obtained only slightly, we have a class of determinations which are better named solidification point methods, depending for their values upon temperature readings at constant time intervals from a thermometer immersed in a slowly cooling wax. Curves drawn from these data show flat points at the solidification temperatures of the prime ingredients of the wax mixture. In this paper we are concerned with the simpler melting point determinations.

## Apparatus and Method

For comparative melting points of a series of wax mixtures, it is very desirable that a number of related determinations be made at one time. This ensures that the rate of heating, the amount of stirring or agitation, and all other factors shall be exactly the same for the entire series. To this end the apparatus illustrated in Figure 1 has been devised.

The apparatus consists of a brass plate  $12 \times 3$  cm. suspended in the center of a 2-liter beaker containing 1700 cc. of water.



FIGURE 2



# Experimental

Using the method described above, melting points of various commercial waxes were determined. Then in a single series the melting points of binary mixtures of various combinations of these were determined at 10 per cent intervals of composition. Tertiary mixtures were then prepared according to predetermined compositions, as explained below, and their melting points determined in series.

Melting point curves of the binary wax mixtures are to be found in the three narrow graphs surrounding each of the triangular graphs. The triangular graphs, of course, represent all possible ternary mixtures of the waxes indicated. Since only compositions can be plotted, a single curve connects all mixtures melting at one specific temperature. The melting point in degrees Centigrade for each curve is indicated thereon. In general, a curve is drawn for every 2.5° rise in melting point, and the curves then may be compared to the altitude lines on a contour map. Each apex of the triangle represents 100 per cent of the wax indicated, and also 100 per cent of the indicated wax for the binary graph adjoining. An inspection of the curves will make this evident.

Each side of the triangle represents all binary mixtures of the two waxes indicated at the ends of the line. From the binary melting point data we may select binary mixtures melting at, let us say, 62.5°, 65°, 67.5°, 70°, and 72.5° C. By drawing a line on the triangular graph between two sets of binaries that have the same melting point we obtain suggested compositions of ternary mixtures for that melting point. Compositions are chosen at uniform intervals over the length of the line and the melting points of the ternary mixtures determined. For a very short line one ternary mixture is sufficient, while for a long line 4 or 5 ternary mixtures are used. A number of checks were made on each mixture and checks

within 0.5° C. were required. In no case was it found that the suggested composition failed to have the required melting point within the limits of experimental error.

# Results and Conclusions

The complete picture of the most interesting and valuable results obtained in this study is shown here graphically. A careful study of these graphs will materially assist one in any investigation of the characteristics of the waxes used in these melting point studies. Knowing the qualitative composition of a ternary mixture of waxes, the melting point of this mixture will enable one by use of these graphs to determine the approximate quantitative composition of the mixture with a minimum of other data. Likewise by use of the graphs, mixtures of waxes of any desired melting point can readily be prepared. The practical usefulness of these graphs to anyone pursuing studies of waxes far surpasses any theoretical discussion which might be set down here based on the results.

Nevertheless some of the outstanding characteristics evidenced by certain waxes are worthy of comment. It will perhaps seem striking at first sight that the isothermals actually are straight lines within the limits of experimental error. This substantiates the idea that wax mixtures are true mixtures and that new chemical compounds are not formed. Because of the comparative chemical inertness of the esters and hydrocarbons making up most waxes, this is to be expected. The effectiveness of small amounts of carnauba in raising the melting points of individual or mixed waxes is noted in Figure 3 (left and center). This is shown in the triangular graphs by the packing of the isothermal lines near the bottom of the graphs. In these two graphs, the contour line conception of the isothermals can be best appreciated, and it is not difficult to visualize the third dimension which these lines

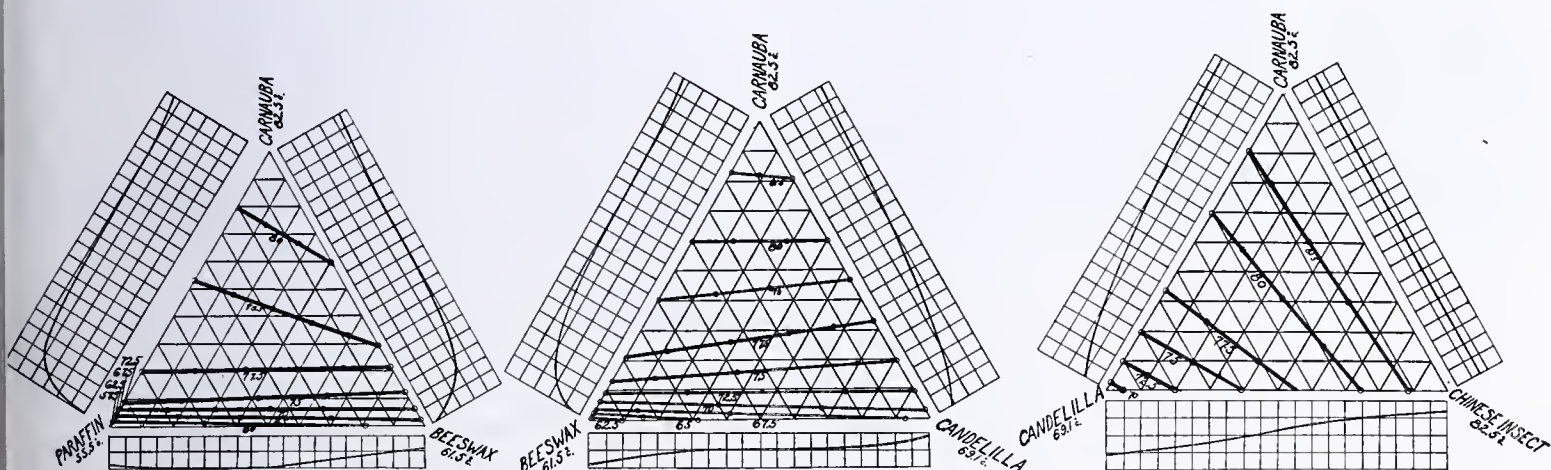


FIGURE 3. MELTING POINT GRAPHS

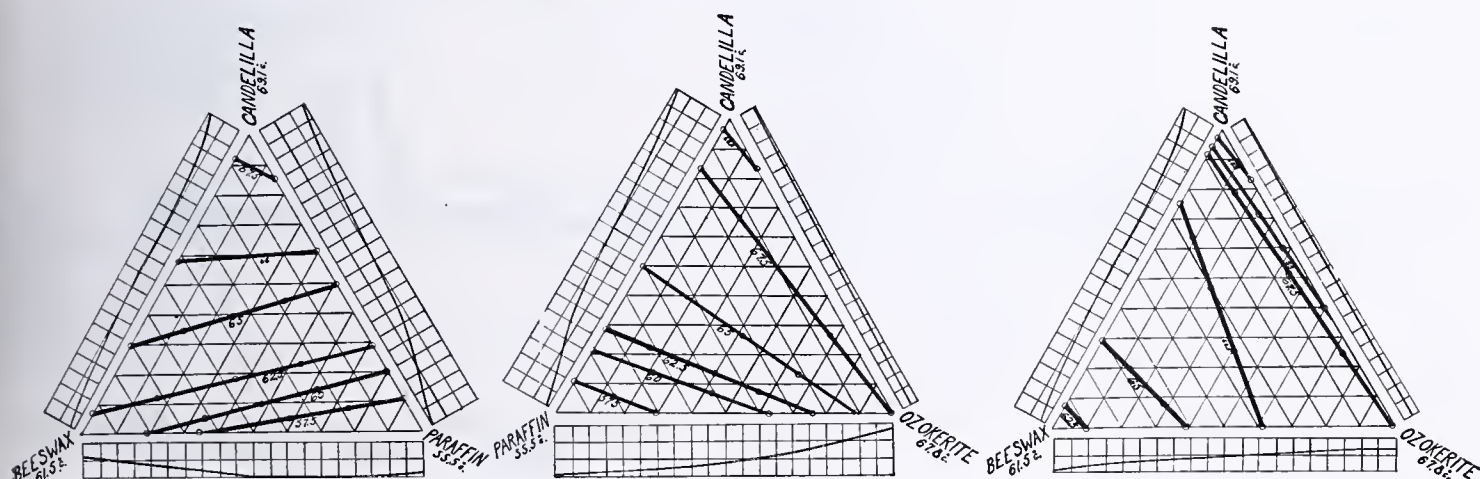


FIGURE 4. MELTING POINT GRAPHS



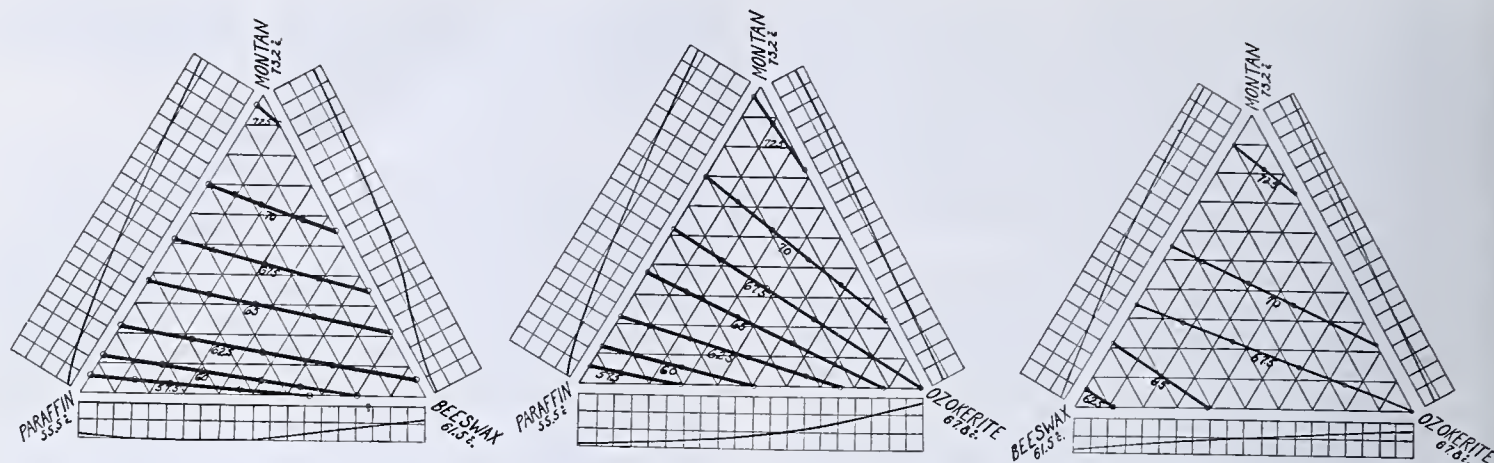


FIGURE 5. MELTING POINT GRAPHS

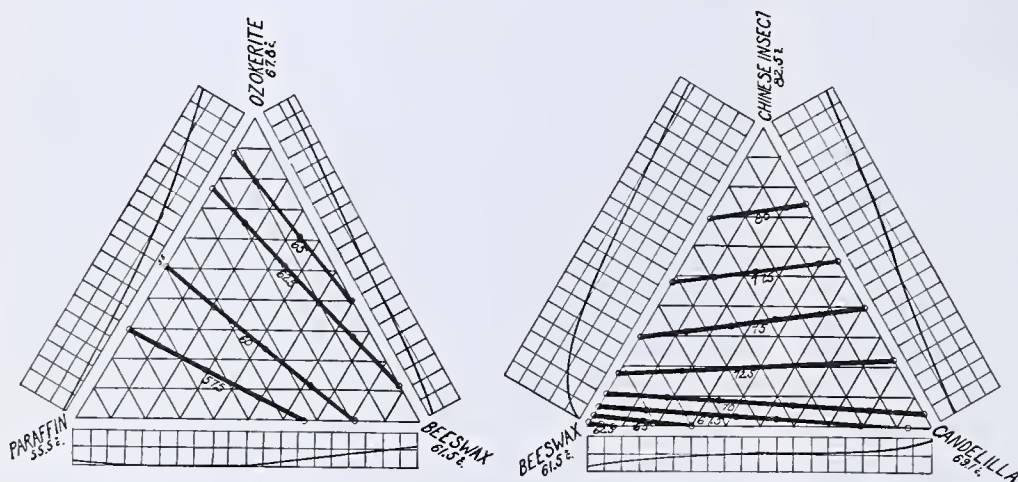


FIGURE 6. MELTING POINT GRAPHS

portray, especially by using the adjacent binary graphs as profile maps.

The only other wax approaching carnauba in its effectiveness in quick melting point rise is Chinese insect wax, whose effect on beeswax is shown in Figure 6.

The fact that the isothermal lines are not parallel in any instance quickly establishes the fact that the effect of any in-

dividual wax on the melting points of two other waxes is never proportionally the same, but is specific. This is also shown by the dissimilarity in the shape of the various binary mixture curves. A striking example of the effectiveness of each of two waxes in altering the melting point of the other when present in small quantities is shown in the binary curve for beeswax and candelilla (Figure 6). A diametrically opposite effect is shown in the case of candelilla and Chinese insect wax on the same graph. Many other equally interesting characteristics of the individual waxes could be pointed out.

Since the results produced here graphically represent a large amount of careful and tedious work, it is hoped that these graphs may prove to be a useful tool to many readers.

#### Acknowledgment

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## A One-Piece Standard Pipe Tee Piezometer Ring

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THE static pressure of a liquid flowing in a pipe line can be measured by a manometer. Connection of the manometer to the pipe ordinarily involves the installation of a ring piezometer or the tapping of the pipe. A ring piezometer, a circumferential ring manifold with four or more holes, is supposed to give an average static pressure, while the single tapping gives a reading for only the tapped point. But the ring piezometer is costly of construction and not easy to attach; often it is built in with the equipment, as in the case of the Venturi meter.

To overcome the complications and costliness of the ring piezometer, Baker and Komich (1) substitute a circumferential slot for the numerous tapped holes, using a single tapping of the pipe. This modified ring requires fittings totaling five threaded joints, one of which is through the thin curved wall of the nipple where the lead-off tap is located.

A simpler arrangement with but three joints and a standard

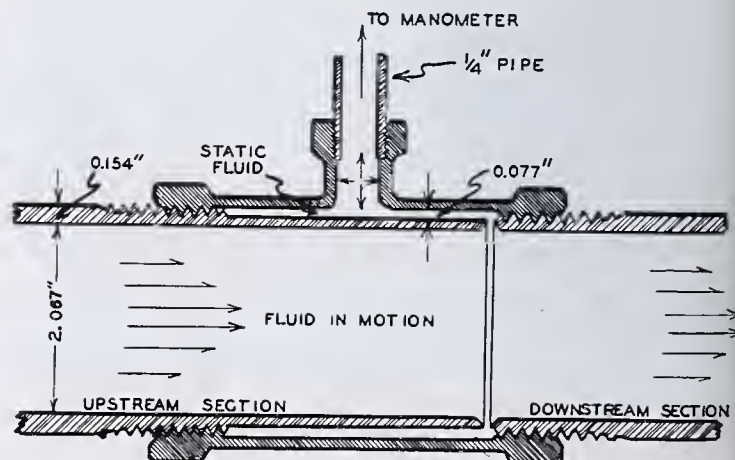


FIGURE 1. STANDARD TWO-INCH REDUCING TEE PIEZOMETER RING



outlet instead of a tapping through the pipe wall can be used. Figure 1 shows specifications for a standard 2-inch piping, but the same order of magnitude of clearances is obtained with other pipe tees and piping. The static flow connection from the flow pipe to the manometer consists of an outlet reducing tee. The tee is of the same size as the flow pipe with a nominal 0.25- or 0.125-inch pipe outlet. One end of the flow pipe is screwed into the tee, so that it just emerges into the inner chamber of the tee. The other end is threaded to a length that will allow it to be screwed onto the tee, and to approach the other pipe to within 0.05 inch. The threads on the longer threaded pipe are removed by machining or filing,

leaving only those threads that are engaged by the female threads of the tee. Thus a static fluid chamber is provided between the interior walls of the tee and the outer walls of the penetrating pipe. This annular chamber connects by means of the slot to the flow pipe and by means of the reducing outlet to the manometer.

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RECEIVED November 30, 1937.

# High-Vacuum Gas-Analysis Apparatus

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A simple method is described for the accurate fractional analysis of light hydrocarbons, using high vacuum in the order of 1 mm. of mercury absolute.

The separation is accomplished in a condenser train with temperatures controlled by liquid air. Unusual accuracy is obtained because of the high vapor pressure

ratio of the components at the point of separation. Individual components are determined within 0.02 to 0.1 per cent, depending on their concentration in the original sample.

Results obtained by this method have been used for equipment design and plant control over a period of years.

THE conventional type of apparatus for the separation of a low-boiling hydrocarbon mixture into its individual components employs a fractionating column usually operating at pressures ranging from atmospheric down to 100 mm. mercury absolute. This type of apparatus has found wide acceptance in the oil and gas industries and is adaptable to the analysis of a wide range of gaseous and low-boiling hydrocarbon mixtures.

Another type of apparatus has been used by this laboratory for several years and is believed to offer certain advantages in the analysis of hydrocarbon gases and vapors. Fractionation effected in this apparatus at low pressures by means of a series of simultaneous partial distillations and condensations through a series of tubes, maintaining a temperature gradient from tube to tube.

TABLE I. VAPOR PRESSURE RATIOS

(Working under normal pressures)

Separation	High-Vacuum Apparatus	Standard Column
Methane-ethane	2000	480
Ethane-propane	100	13
Propane-isobutane	12	4.5
Isobutane-n-butane	5	2
n-Butane-isopentane	15	3.5

Some of the advantages claimed for this procedure are the following:

1. A small gaseous sample, nominally 150 cc., is sufficient for complete analysis, thereby eliminating the use of expensive high-pressure bombs or large bulky low-pressure containers.
2. Traces of material at the ends of the distillation are determined with unusual precision—for example, small amounts of heavy hydrocarbons in absorber residue gases may be determined 0.02 per cent and light hydrocarbons in stabilizer residues may be detected within 0.1 per cent based on the original sample.
3. Supplementary tests such as oxygen determination, bromination of unsaturates, slow combustions, etc., may be made on fractions without removing the sample from the apparatus.
4. The time required for an analysis is only about 2.5 hours.

The ease of separation of two hydrocarbons varies directly with the ratio of their vapor pressures at the particular temperature employed. This ratio increases materially as the temperature is reduced (Table I); therefore, it is highly desirable to effect a separation at the low temperatures attainable under high vacuums.

For several reasons it is difficult to operate the usual form of low-temperature column at pressures in the order of 1 mm. of mercury. The vapor capacity of small diameter columns at 1 mm. of mercury or less is markedly reduced, so that the time required to complete an analysis is greatly extended. Small fluctuations in pressures at these high vacuums greatly affect the fractionation and accuracy of the results. Shepard and Porter (1) employed a high-vacuum apparatus for the analytical separation of gaseous hydrocarbons by a series of fractional condensations and distillations through a condenser train without the use of reflux. The apparatus described in this article depends essentially upon the same principle as the Shepard and Porter method, but is of different design, requires less time per analysis, and gives results which are thought to be of the same precision.

### Apparatus

The separations are effected at a pressure of less than 1 mm. absolute in a train of four condenser tubes held accurately to temperature by the procedure described below, using liquid air as the cooling agent.

The apparatus is constructed entirely of Pyrex glass with all fused joints except in the Orsat section where substantially atmospheric pressures are used and danger of leaks is small. It consists (Figure 1) essentially of a condenser train for the low-temperature separation of the hydrocarbons, an internal high-vacuum pumping system for transferring sample and fractions, a McLeod gage for determining the pressure in the system, a constant-volume buret for measuring both sample and fractions, drying tubes, and an Orsat system for running supplementary tests.

As the apparatus does not work well with liquid samples, a



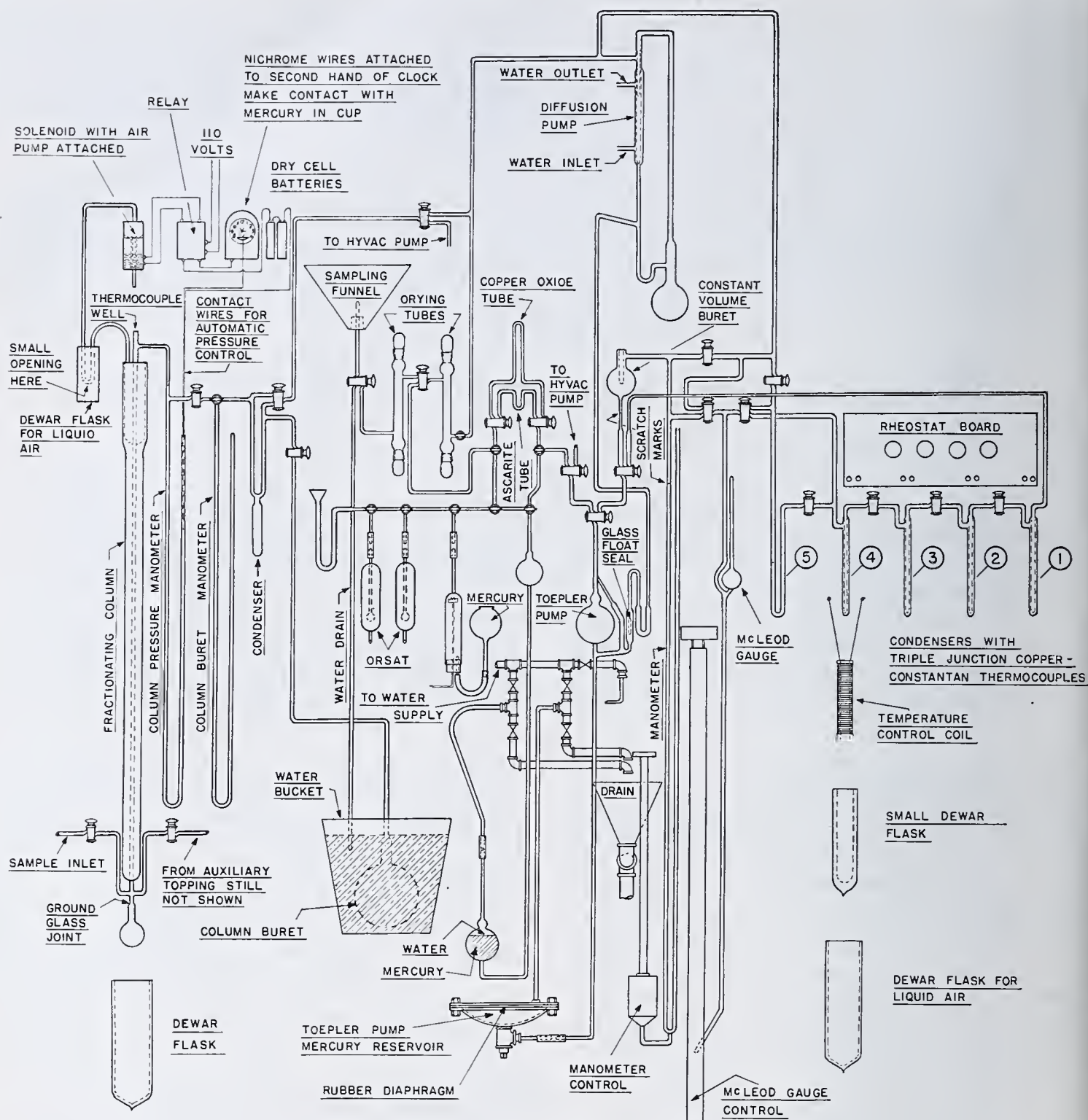


FIGURE 1. DIAGRAM OF APPARATUS

fractionating column assembly is incorporated into the system for the analysis of liquids. This is similar to the conventional gas-analysis apparatus. The column itself (Figure 1) is of the usual type, vacuum-jacketed, silvered, and provided with a spiral wire packing. A 2-liter flask immersed in a water bath serves as a gas buret to measure the overhead vapor. An open-end and a closed-end manometer measure the column and buret pressure, respectively. A topping still (not shown) is sometimes used to top heavy samples such as crude oils, absorption oils, heavy gasolines, etc., the tops then being analyzed in the column.

A connection to the diffusion pump makes it possible to transfer fractions from the column apparatus to the high-vacuum apparatus for further analysis, or to the Orsat for determination of unsaturates. Small amounts of propane in stabilizer bottoms may be very accurately determined by removing the propane and a small part of the butane in the column and reanalyzing this mixture in the high-vacuum apparatus. The apparatus is made entirely of Pyrex glass with all joints fused; consequently leaks are rare even when operating at low pressures.

An efficient and trouble-free device for the automatic control of column pressure is shown. A U-tube with a very small hole in the bottom is partially immersed in liquid air, which slowly

runs into the tube until the inside level reaches the outside level. When a puff of air is blown through the U-tube by the solenoid-operated air pump, the liquid air in the tube is blown into the reflux condenser of the column, the amount of liquid depending upon the depth of immersion of the tube. The air pump is operated by the 110-volt circuit from a relay, which in turn is actuated by a dry-cell circuit. The dry-cell circuit is interrupted by contact wires in the open-end column manometer and a clock operated circuit breaker in series. As long as the mercury is high enough in the open end of the manometer to close the circuit across the contact wires, a shot of liquid air will be delivered every 10 seconds until the mercury has dropped sufficiently to break the contact.

The operation of a liquid fractionating column is familiar to most gas chemists. The procedure for the analysis of liquids is therefore not described.

### Analysis of Gases

The apparatus is evacuated to a pressure of 0.001 mm. of mercury or lower and all cocks are closed. A clamp-top bottle containing the gas sample is inverted in the sampling funnel which



is filled with water, and the bottle is unstoppered and slipped over the rubber stopper at the bottom of the funnel. Any water in the bottle is drawn off through the water drain. As the constant-volume buret manometer is of the open-end type, it is necessary to take a blank reading before starting the analysis. This is done by setting the mercury on the buret side of the manometer at the scratch mark and then reading the level on the other side. Gas is admitted to the pumping system through the drying tubes and thence to the constant-volume buret, using the Toepler pump to bring the pressure up to atmospheric. The sample cock is closed and the residual gas in the system pumped out to the Hyvac pump and discarded. A pressure and temperature reading, along with the blank pressure reading previously taken, evaluates the quantity of gas in the buret.

**REMOVAL OF CARBON DIOXIDE.** The sample is pumped into the Orsat leveling bottle and allowed to pass slowly through the ascarite tube, through one drying tube, and to the diffusion pump inlet where it is transferred back into the buret and measured. The loss represents carbon dioxide or other acidic gases. One pass through the Ascarite tube is sufficient to remove all the carbon dioxide.

**REMOVAL OF METHANE AND LIGHTER CONSTITUENTS.** The temperature-control coils, which are copper cylinders closed on one end and wound with resistance wire, are slipped over the condenser tubes and fastened to the binding posts on the rheostat board which form a support as well as an electrical contact for the coils. They are filled with light gasoline to afford contact and are cooled by immersing in liquid air. (Holders for liquid air flasks are not shown.) The condenser tubes are provided with triple-junction copper-constantan thermocouples having an ice and water cold junction and connected through a multipoint switch to a potentiometer. Condensers 5 and 4 are immersed in liquid air throughout the methane removal. When condenser 5 reaches a temperature of  $-160^{\circ}\text{C}$ ., the small Dewar flask is slipped over the condenser coil and then immersed in liquid air. No. 3 rheostat is then adjusted so that the heat input through the resistance coil just balances the heat loss through the small Dewar flask to the liquid air and the temperature of the condenser is held constant at  $-160^{\circ}\text{C}$ . In a similar manner condenser 2 is held at a temperature of  $-142^{\circ}\text{C}$ ., and No. 1 at  $-128^{\circ}\text{C}$ .

The sample is transferred to condenser 1 and then admitted slowly to Nos. 2, 3, 4, and 5 in succession. The sample has now distributed itself along the condenser train. The heavier constituents are condensed in No. 1, and of the lighter constituents, only a part of the methane fraction has been able to reach No. 5.

The McLeod gage is opened to No. 5, which is then opened slightly to the diffusion pump inlet. As the methane fraction slowly escapes to the pumping system, it is pumped into the buret by running the mercury up into the Toepler pump occasionally. As the pressure is reduced in No. 5, the condensed material begins to redistribute itself in the train, moving from right to left. There is a fractional distillation from each condenser, followed by a fractional condensation in the next. When the pressure in No. 5 has been reduced to 0.25 mm. of mercury, the ethane separation is considered complete. All the gas in the pumping system is pumped into the buret and measured and all the cocks are closed.

TABLE II. SEPARATION TEMPERATURES AND CUTTING PRESSURES EMPLOYED WITH HIGH-VACUUM APPARATUS

Separation	Pressure Mm.		Condenser				
			No. 5	No. 4	No. 3	No. 2	No. 1
				$^{\circ}\text{C}$ .	$^{\circ}\text{C}$ .	$^{\circ}\text{C}$ .	$^{\circ}\text{C}$ .
ethane-ethane	0.25	Liquid air temperature		-175	-160	-142	-128
ethane-propane	0.1	Liquid air temperature		-160	-143	-128	-113
propane-butane	0.1	Liquid air temperature		-142	-128	-113	-100
butane-pentane	0.1	Liquid air temperature		-117	-103	-90	-77

**ANALYSIS OF FIXED GASES.** The methane fraction is transferred to the Orsat section and tested for oxygen, using an alkaline pyrogallol solution. If it is desirable to test for carbon monoxide, hydrogen, or nitrogen, a slow combustion analysis is run on a portion of the methane fraction or a cuprous chloride pipet may be inserted in the Orsat train for the absorption of carbon monoxide. The copper oxide tube may also be used for the determination of carbon monoxide and hydrogen. When all desired tests have been made on this fraction, it is pumped out by the Hyvac pump and discarded.

**DETERMINATION OF ETHANE AND ETHYLENE.** For the removal of the ethane fraction, condenser 5 is used merely as part of the pumping system and the final separation takes place in No. 4. No. 4 is brought up to a temperature of  $-160^{\circ}\text{C}$ ., No. 3 to

$-143^{\circ}\text{C}$ ., etc. (Table II). The McLeod gage is opened to No. 4 and ethane-ethylene is removed like methane until the pressure in No. 4 has been reduced to 0.1 mm. of mercury. The cocks on the condenser train are closed, No. 5 is allowed to come to room temperature, and the ethane-ethylene fraction is pumped into the buret and measured. The fraction is then transferred to the Orsat section, treated with saturated bromine water to remove unsaturates, scrubbed with caustic, and transferred back to the buret, and the ethane is measured. The loss represents ethylene.

**REMOVAL OF HEAVIER HYDROCARBONS.** The heavier fractions are removed and tested for unsaturates in the same manner, except that a different set of temperatures is used for each fraction (Table II).

**MEASUREMENT OF RESIDUE.** As the pentane and heavier residue fraction is easily condensed, it is not desirable to put it through the pumping system into the buret. For this reason the capacity of the condenser system has been calibrated with respect to the buret. This permits the residue to be measured in two different ways. When the residue is small, as in the case of a dry gas, it is measured directly in the condenser system by means of the McLeod gage. This affords a very accurate measurement. When the residue is too large to be measured in this manner, the condenser system is opened to the buret and the pressure on this combined system measured by the buret manometer.

## Discussion

**SPEED OF ANALYSIS AND LIQUID AIR REQUIRED.** The fractional analysis consumes about 2.5 hours in the hands of an experienced operator. If absorption analysis or the other supplementary tests are necessary, more time is required. Liquid air consumption is from 1.5 to 2 liters per analysis.

**PRECISION OF ANALYSIS.** On two check analyses, methane will ordinarily check to about 0.1 per cent (basis original sample), and ethane, propane, and butane to less than 0.1 per cent. In the case of very dry gases the pentane and heavier fraction will usually check within 0.02 per cent, but on heavy gases containing considerable pentane and heavier, a check within 0.1 per cent is normal (Table III).

TABLE III. CHECK ANALYSES

	Lean Gas		Rich Gas	
	Original	Check	Original	Check
Methane	88.17	88.08	15.70	15.75
Ethane	6.15	6.20	17.42	17.32
Propane	3.53	3.56	33.72	33.74
Butanes	1.50	1.53	27.66	27.75
Pentanes	0.65	0.63	5.50	5.44
	100.00	100.00	100.00	100.00

Hundreds of analyses by this method have been successfully used in the preparation of material balances, in the design and testing of equipment, in checking the composition of gases and liquids in equilibrium, and for general plant control purposes.

**GASES ANALYZED WITH THE APPARATUS.** The high-vacuum fractionation train, as such, is used for the separation of hydrocarbon gases only. Fixed gases are removed along with methane and are thus separated from the heavier hydrocarbons. This makes supplementary tests, such as slow combustion, Orsat, etc., more easily accomplished. By use of proper pipets and reagents in the Orsat system, in conjunction with the low-temperature fractional analysis, almost any gaseous mixture that will not attack mercury may be analyzed. The gases most commonly determined include hydrogen, carbon monoxide, oxygen, nitrogen, helium (charcoal absorption tubes, not shown, are provided for the determination of helium), carbon dioxide, hydrogen sulfide, methane, ethylene, ethane, propylene, propane, total butylenes, butanes, and pentane and heavier residue. All these determinations are made in the one integral apparatus with none of the danger of loss or contamination of sample which would be encountered in transferring from one apparatus to another.

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# Modern

# Laboratories

## The Microchemical Laboratory of the American Medical Association

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IN ORDER to apply microchemistry to the various problems of chemistry related to pharmacy (2, 3, 5, 8, 22, 26, 27), medicine, and clinical chemistry (19, 21), the American Medical Association established a microchemical laboratory. It is the purpose of this paper to describe this laboratory and some of the methods used in its manifold duties to the association and to physicians.

The microchemical laboratory is located in a room  $3.5 \times 3.3 \times 6$  meters ( $10.5 \times 10 \times 18$  feet). At one end of the room are the vestibule for entering and leaving the room and the cases for two balances (1, 9). These protection cases are suspended at the sides only. The balances themselves are supported independently of the protection cases; the former rest on type-metal slabs that in turn rest on corrugated lead sheets, which finally are supported by brackets on the back wall. Laboratory work tables occupy the rest of the wall space except for a small sink in a corner at the opposite end. The tables are equipped with gas, water, and electrical outlets and drains. The depths of the drawers vary and are relatively smaller than are the drawers in a laboratory for macrochemistry. For convenience, the drawers have been fitted with partitions of heavy Cellophane, and the glassware in the cupboards is kept separated with strips of balsam wood.

In order that microchemical determinations of all kinds may be carried out regardless of the outside weather conditions, the temperature and humidity of the room are controlled. [The temperature of  $22.22^\circ\text{C}$ . ( $72^\circ\text{F}$ .) and the 55 per cent relative humidity seem to be the average of different laboratories. Private communications with Doctor Hayman of Merck & Co., Inc., Rahway, N. J.] The temperature is usually maintained at  $22.22^\circ\text{C}$ . ( $72^\circ\text{F}$ .), a variation of  $\pm 0.28^\circ\text{C}$ . ( $\pm 0.5^\circ\text{F}$ .)

being allowable. The relative humidity is set at 55 per cent with an operating variation of  $\pm 1.5$  per cent.

For efficiency in operation, the room is elaborately insulated. The floor, ceiling, and walls are covered with 10 cm. (4 inches) of cork and 5 cm. (2 inches) of cement. To prevent the loss of large volumes of conditioned air, the room is entered through the vestibule already mentioned. The single window is fitted with double (Thermopane) glass and is covered at will with a venetian-type shade.

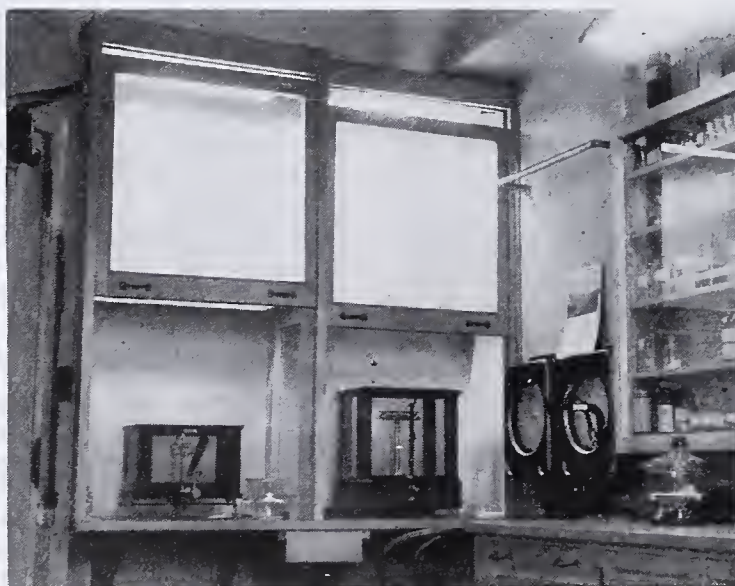
The machinery for maintaining constant temperature and humidity includes the air-conditioning system and the controls

The air-conditioning machinery is located on the floor below the microchemical room. A mixture of air to be recirculated and fresh air is cooled in a water spray maintained at approximately  $10^\circ\text{C}$ . ( $50^\circ\text{F}$ .). In this way the air is washed, cooled, and dehumidified. After leaving the spray the air is humidified suitably with a water-covered steam coil and then heated to the proper temperature by another steam coil.

The air is delivered to the room through a series of holes in a duct, which runs the length of the room near the ceiling. The air is returned to the conditioner by means of a large duct that takes the air at the floor from the same side of the room as the air intake. A smaller return duct opens on the opposite side

of the microlaboratory 1.5 meters (4 feet) above the floor and guides a small amount of air past the master controlling instruments. This arrangement of the inlet and outlet ducts causes most of the air to cross the room as it enters at the ceiling and to recross at a lower level as the air approaches the outlet duct. The relatively small amount of air that enters the small duct after crossing the room once tends to make the system quick to react to changes in temperature and humidity. The system was calculated to deliver 14.16 cu. meters (500 cubic feet) of air per minute but something less than this volume is usually used.

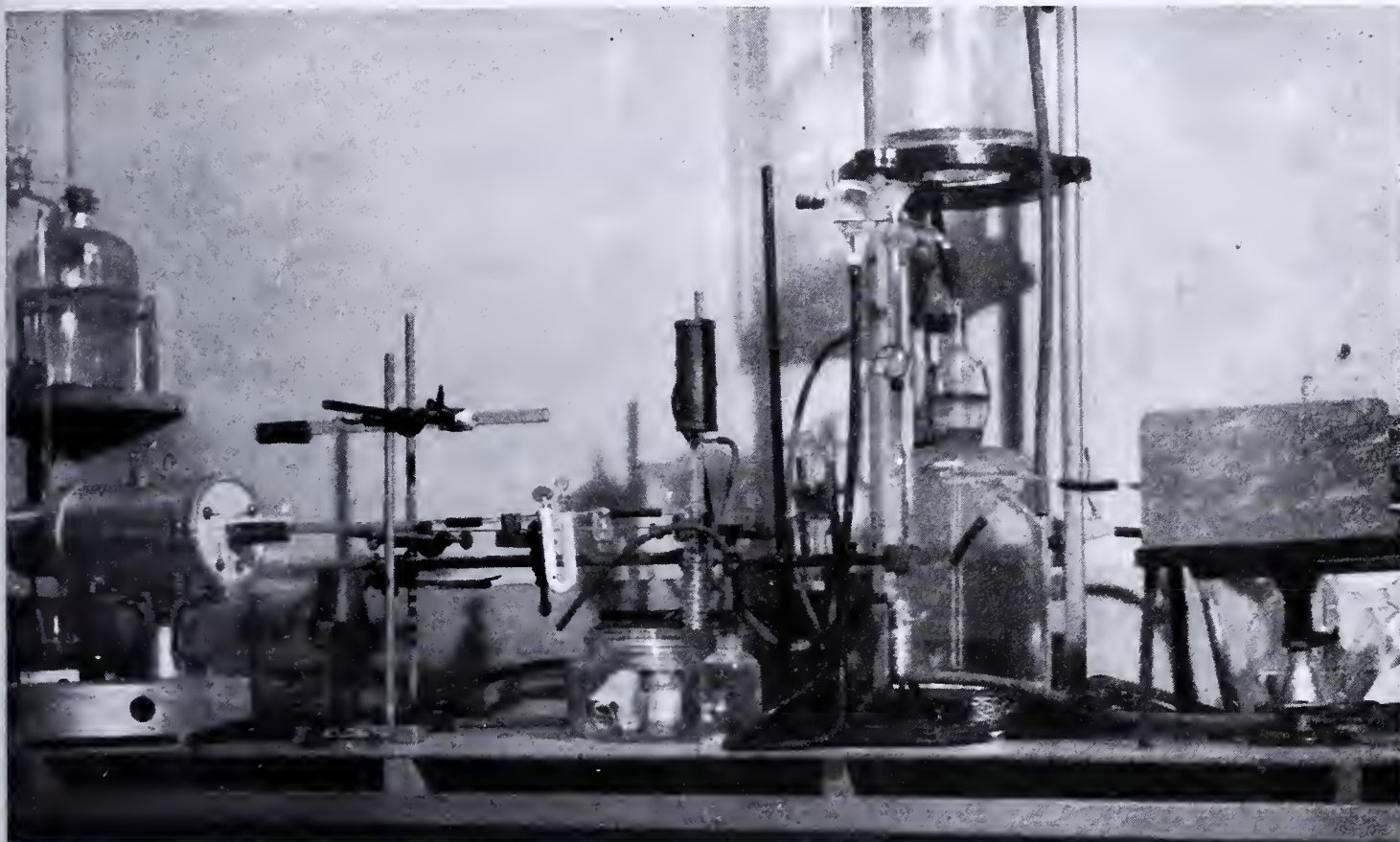
The controlling instruments are all activated by compressed air. The master instruments, a thermostat and a humidostat, are located in the microchemical laboratory; they record the temperature and the relative



CASES FOR BALANCES

Protection cases are suspended at the sides only; the balances are supported independently of the cases.





APPARATUS IN MICROCHEMICAL LABORATORY OF AMERICAN MEDICAL ASSOCIATION

humidity. The other controlling instruments include electrical switches activated by compressed air, steam valves, water valves, and air dampers. They are mounted on the air-conditioning machinery.

### Microchemical Equipment

The microchemical laboratory is equipped for organic and inorganic analysis, including a room for spectrographic and other optical and physical work (16). The following microchemical apparatus was found to be essential: carbon and hydrogen (Pregl); nitrogen (Pregl); Kjeldahl, all-glass; reflux (Pregl); acetyl (Friedrich); methoxyl (Vieböck-Schwappach); methylimide (Friedrich); and inorganic analysis (the methods of Behrens-Kley, Emich, Pichler, Feigl, and Lamot are used according to the problem). A Kuhlmann microbalance, a semimicrobalance, and a Starke and Kammerer torsion balance constitute the necessary weighing equipment; microextractors and general microglassware, with a lot of ground-glass joints, are useful. Most of the heating units are electrified to minimize the heat radiation and the large amounts of water, carbon monoxide, and carbon dioxide, given off by gas flames. A Kofler melting point microapparatus, together with a polarizing microscope, aids in general drug identification (12). An ultraviolet lamp properly fitted with filters for fluorescence analysis provides the necessary light for chromatographic adsorption analysis (30), capillary strip analysis (15, 24), and the fluorescence microscope (4, 7a, 7c, 20).

The Kofler melting point apparatus is a valuable instrument in identifying minute quantities. A general description of a typical problem will best illustrate its use.

A few drops of a liquid, suspected to contain a certain barbiturate, were evaporated on the Fisher plate of Kofler's apparatus at low temperature and under vacuum. After the evaporation the dry solid was sublimed at atmospheric pressure. The first sublimate was resublimed and the melting point recorded. To identify the barbiturate in the liquid, the capillary strip method

was used (10, 17, 23, 25). Two filter papers, 15 cm. long and 1 cm. wide, were immersed to a depth of 0.5 cm. in microbeakers, one of which contained 3 cc. of the liquid under investigation and the other the same volume of a liquid resembling the original material in aroma and taste but containing a small amount of the suspected barbiturate. After contact for 3 hours the filter papers were examined under ultraviolet light. Both exhibited a fluorescence of the same bluish white shade and intensity. Another small portion of the liquids was adsorbed on a microcolumn of aluminum oxide (6), and the chromatograms were developed. (The best solvent, developer, eluting agent, and adsorbent for barbiturates have to be determined in each case.) Both chromatograms showed the same color variation under fluorescent light.

A quantitative determination of the barbiturate was achieved by soaking a small filter paper with 1 cc. of the liquid, drying it in a stream of warm air, and extracting it in a micro Soxhlet. (A hair dryer with a heating element is a very useful tool in micro-work.) The extract was cautiously evaporated and made alkaline, then shaken out with chloroform in a small pipet. The alkaline liquid was acidified and again extracted with chloroform. The chloroform layer was evaporated in a suitable dish and the residue weighed. The melting point (determined on the microapparatus) of the sublimate from the weighed product and the crystallographic properties of the crystals (11, 13) proved to be that of the barbituric acid in question. This method is also applicable in cases of identification of barbiturates in biologic liquids like urine and spinal fluid (14, 18, 23, 29).

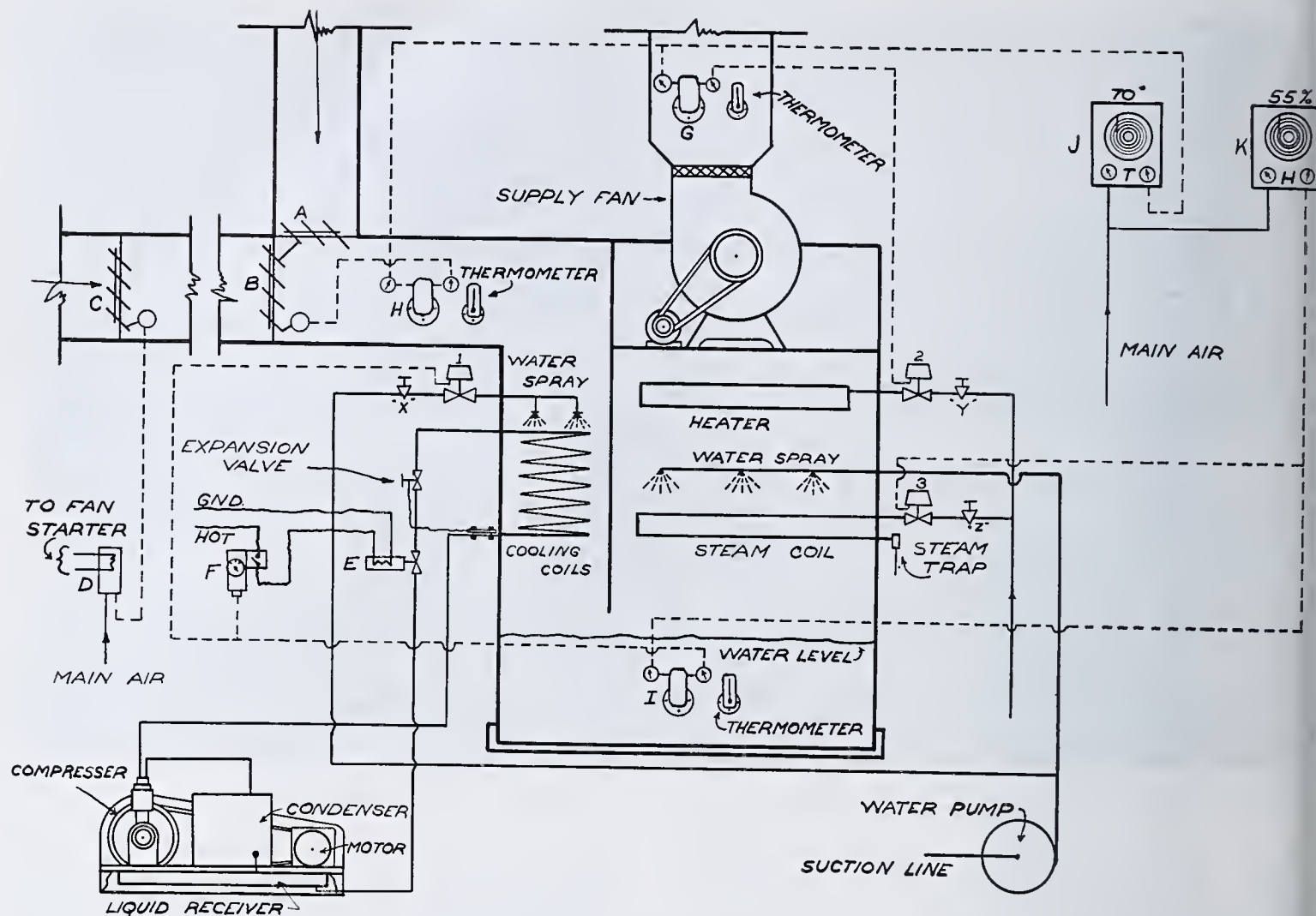
### Summary

The American Medical Association microchemical laboratory and its air-conditioning system are described. A list of apparatus and procedures useful in pharmaceutical analysis is given. Literature references for forensic work, especially for identification of barbiturates, are included.

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AIR CONDITIONER

- A. Return air damper. Air pressure to close damper  
 B. Fresh air damper. Air pressure to open damper  
 C. Auxiliary fresh air damper. Air pressure to open damper  
 D. Solenoid air valve. Air pressure in branch line when coil is energized  
 E. Solenoid liquid valve. Open to flow when coil is energized  
 F. Adjustable pressure switch. Contacts open with air pressure  
 G. Insertion thermostat in fan discharge duct. Air pressure on branch line on rising temperature  
 H. Insertion thermostat in mixture of fresh and return air. Pressure in branch line on rising temperature  
 I. Immersion thermostat in cold-water pan. Air pressure in branch line on lowering temperature  
 J. Temperature recorder and controller located in conditioned space. Air on branch line on rising temperature  
 K. Humidity recorder and controller located in conditioned space. Air on branch line on lowering relative humidity  
 1, 2. Automatic water valve and steam valve  
 3. Automatic steam valve. Air pressure to open valve  
 X, Y, Z. Hand valves

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# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION

Harrison E. Howe, Editor

## Determination of Nickel in Alloy Steels

### A Photometric Titrimeter

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THE volumetric determination of nickel in steel as proposed by Moore (6) has been investigated so often that further studies in this field may appear to be unnecessary. However, the data are not very consistent, and apparently no effort has been made to find what conditions are necessary to yield results on a basis of  $1\text{Ni} = 2\text{Ag}$ .

Johnson (3) has reported extensively on the subject, although his data do not include a study of such conditions as the permissible limits of nickel concentration, the amount of excess ammonia, and the range of temperature. The procedures recommended by Lundell, Hoffman, and Bright (5) and by the American Society for Testing Materials (1) are almost identical and are presumably the average conditions used by a large number of analysts in the field. Recently, Peters (8) has applied the cyanide titration for nickel to nickel-chromium alloys, but fails to specify the temperature at which the titration should be made. The temperature is just as important as the amount of excess ammonia, as is shown below. Kolthoff (4) considered the optimum conditions necessary for the determination of alkali cyanides by titration with silver nitrate in ammoniacal solution, using mercuric iodide as an indicator. He recommended 4 to 6 ml. of 5 N ammonia in excess, and 0.2 gram of potassium iodide per 10 ml. of solution.

Electrolytic deposition is recommended for unimpure nickel determinations in high-nickel steels (2), but this method cannot be used for control in a steel-making process because of the time required. The dimethylglyoxime method (1, 5) consumes much less time but has the disadvantage of requiring small samples (aliquot portions) for high-nickel alloys. An additional factor, too often neglected, is the instability of the nickel dimethylglyoxime.

The cyanide method, while rapid, is not entirely satisfactory if the end point is judged by visual means. Partridge (7) has demonstrated the use of the photoelectric cell as an indicator in precise titrations. In the present study, it was decided to employ the photronic cell for the determination of the end point in the cyanide titration method for nickel.

#### Apparatus

A modified arrangement of Partridge's apparatus was assembled (Figures 1 and 2), using a Leeds & Northrup students' type of potentiometer to measure the e. m. f. of the photronic cell. The potentiometer was used only to obtain the curves shown in Figures 3 and 4. All other titrations in this investigation were made with ordinary radio potentiometers that were made an integral part of the completed apparatus.

The galvanometer used was a Leeds & Northrup instrument of the enclosed lamp and scale type with a sensitivity of 0.02 microampere per mm. division. Figure 1 shows a schematic diagram of the apparatus along with the electrical circuits used. The lamp housing has a small 110-volt 15-watt concentrated filament lamp with a reflector mounted rigidly in one end of a brass tube. The lamp voltage is kept constant with a Raytheon voltage regulator of 60 watts' capacity. The manu-

facturer claims an output of  $115 \text{ volts} \pm 1 \text{ per cent}$ . These regulators were found much more convenient than storage batteries and have proved sufficiently constant for this type of work. The other end of the lamp housing contains a small lens, 3.5 cm. in diameter, to render the light rays parallel.

The compartment for the glass cell is made of fiber board, 6.3 mm. (0.25 inch) thick, and of such inside dimensions as just to accommodate the glass cell. Its

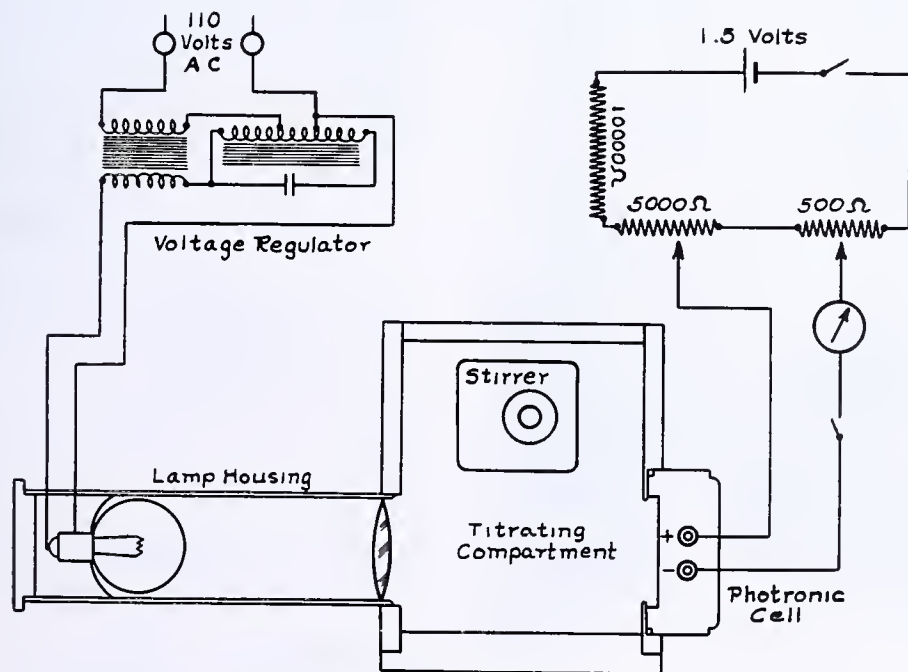


FIGURE 1. DIAGRAM OF APPARATUS



inside height is 14 cm., which is sufficient to shield the solution from stray light. The glass cells are of the museum jar variety with a total capacity of about 0.9 liter. While these cells are not optically perfect, they are nevertheless satisfactory since the potentiometer setting for each titration has its own initial zero. The photronic cell, manufactured by the Weston Electrical Instrument Corporation, is mounted directly opposite the lamp housing with a 3.5-cm. hole for the light to impinge on the cell. This area allows the activation of about 80 per cent of the photronic cell's surface. The stirring apparatus, marketed by the Arthur H. Thomas Company, is of the worm-gear drive type with a hollow spindle through which the glass stirring rod is fastened by a spring clamp. This has the additional advantage that it can be raised and lowered conveniently when changing the glass cells. All burets used were calibrated by the National Bureau of Standards.

### Reagents and Standard Solutions

**CITRIC ACID SOLUTION.** Dissolve 200 grams of citric acid (U. S. P. grade) in 1000 ml. of water.

**SODIUM IODIDE SOLUTION.** Dissolve 10 grams of sodium iodide in 100 ml. of water.

**COPPER SULFATE SOLUTION.** This solution was prepared from a c. p. grade of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and was standardized by precipitating the copper as the sulfide and igniting to cupric oxide. Its strength was adjusted to equal 0.0002 gram of copper per ml.

**COBALT SULFATE SOLUTION.** The cobalt in a c. p. grade of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  was precipitated once as potassium cobaltinitrite (2) in order to remove nickel. The potassium cobaltinitrite was decomposed with nitric acid and the solution fumed with sulfuric acid. It was standardized by precipitating the cobalt with  $\alpha$ -nitroso- $\beta$ -naphthol and igniting to  $\text{Co}_3\text{O}_4$ . Its strength was adjusted to equal 0.0002 gram of cobalt per ml.

**PURE METALLIC NICKEL.** The nickel metal was a special metal prepared by W. A. Wesley of the International Nickel

Company. The purity indicated, by difference, after chemical and spectroscopic examination was 99.98 per cent nickel.

**STANDARD SILVER NITRATE SOLUTION.** Dissolve 5.789 grams of silver nitrate in water and dilute to exactly 1000 ml. One milliliter of this solution is theoretically equivalent to 0.0010 gram of nickel.

**STANDARD SODIUM CYANIDE SOLUTION.** It is convenient to have two solutions on hand: For low-nickel alloys, dissolve 3.4 grams of sodium cyanide in 1000 ml. of water containing 1.0 gram of sodium hydroxide. For high-nickel alloys, dissolve 28.0 grams of sodium cyanide in 1000 ml. of water containing 1.0 gram of sodium hydroxide.

Standardize by applying the method described in the section under recommended procedure. Cyanide solutions change with age and must be checked daily.

### Recommended Procedure

Weigh accurately a 1-gram sample of alloys containing from 5 to 35 per cent of nickel. For alloys containing more nickel, use a weight equivalent to about 0.3 gram of nickel.

Transfer the sample to a 600-ml. beaker, treat with 20 ml. of diluted nitric acid (1 to 1), and heat until solution is complete. Dilute to 300 ml. with cold water and add 60 ml. of citric acid solution. Add diluted ammonium hydroxide (1 to 1) until just alkaline to litmus, and then 5 ml. in excess. Transfer the solution to the glass titrating cell, and add 2 ml. of standard silver nitrate solution and 10 ml. of sodium iodide solution. Dilute to 500 ml. and adjust the temperature to 30° C. Add standard sodium cyanide solution until the solution clears and then about 1 ml. in excess. Adjust the galvanometer to zero. Titrate the excess cyanide with standard silver solution until a permanent deflection of 25 mm. is obtained. A correction for the total amount of silver nitrate used must be made.

Standardize the sodium cyanide solution by titrating an iron-nickel alloy of known nickel content. The calculation of the nickel titer of the cyanide solution is made according to Formula 1. The calculation for the per cent of nickel found is made according to Formula 2.

$$\text{Nickel titer} = \frac{\text{grams of nickel} + (\text{ml. of AgNO}_3 \times 0.0010)}{\text{ml. of NaCN}} \quad (1)$$

$$\text{Per cent of nickel} = \frac{\text{ml. of NaCN} \times \text{Ni titer} - (\text{ml. of AgNO}_3 \times 0.0010)}{\text{weight of sample}} \times 100 \quad (2)$$

Although copper and cobalt consume cyanide, a correction can be made when the amounts are definitely known. The reaction with copper approximates the ratio,  $2\text{Cu} = 7\text{CN}$ , and the nickel equivalent can be calculated by multiplying by the factor 0.807. While the reaction with cobalt is not exactly  $1\text{Co} = 4\text{CN}$ , it may be assumed to be so if the amount present does not exceed 5 mg.

Chromium has no effect on the nickel titer if less than 0.1 gram is present. With high-chromium alloys, a sample that contains less than 0.1 gram of chromium must be taken or else an equal amount must be added to the standard used for determining the nickel titer of the cyanide solution.

### Experimental

The experimental work described below was done to determine the optimum conditions necessary for the development of the recommended procedure. A brief study of the effect of other elements is included.

**CYANIDE vs. SILVER END POINT.** The curves shown in Figures 3 and 4 present comparisons between the nickel-cyanide end point and the excess cyanide-silver end point. The titrations were made on weighed portions of 0.3 gram of pure nickel, 1.0 gram of 30 per cent nickel steel, and 0.4 gram of nickel-chromium (80/20) alloy. The conditions for the titrations were as follows:

The samples were dissolved in 10 ml. each of hydrochloric and nitric acids, diluted to 300 ml. with cold water, and treated with 120 ml. of the citric acid solution. The solutions were neutralized

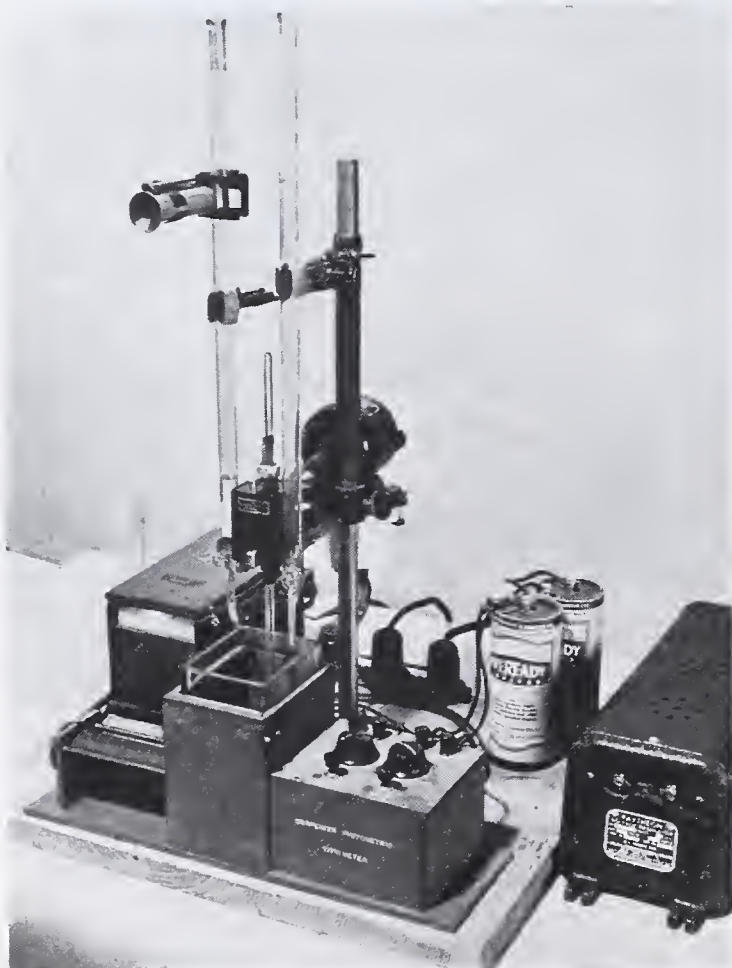


FIGURE 2. ASSEMBLY OF PHOTOTITRIMETER



with 7.5 *N* ammonia, treated with 5 ml. in excess, and diluted to 500 ml., and the temperature was adjusted to 30° C. The solutions were titrated with standard sodium cyanide solution until the maximum point of inflection was reached. A small amount of cyanide was added in excess to show the effect of diluting the background color (iron and chromium citrates). The curves shown in Figure 3 were obtained by plotting the volume of standard sodium cyanide solution against the e. m. f. of the photronic cell.

After titrating with the cyanide, the solutions were treated with 10 ml. of the sodium iodide solution and the excess cyanide was titrated with standard silver nitrate solution. Figure 4 shows the curves obtained by plotting the volume of standard silver nitrate solution against the e. m. f. of the photronic cell.

TABLE I. EFFECT OF AMMONIA CONCENTRATION ON THE REACTION BETWEEN NICKEL AND CYANIDE IONS

(1-gram samples of iron-nickel alloy, 29.96 per cent nickel)

Excess 7.5 <i>N</i> Ammonia per 500 ml. of Solution	NaCN Added	AgNO <sub>3</sub> Used	Nickel <sup>a</sup> Found	Error
ml.	ml.	ml.	Gram	Mg.
Just alkaline	39.41	4.6	0.3000	+0.4
	39.62	6.2	0.3000	+0.4
5.0	39.70	7.0	<i>b</i>	...
	39.65	7.0	....	...
10.0	39.59	6.6	0.2994	-0.2
	39.64	7.4	0.2989	-0.7
20.0	39.57	8.1	0.2977	-1.9
	39.62	8.2	0.2980	-1.6
25.0	39.65	9.2	0.2972	-2.4
	39.60	8.3	0.2977	-1.9

<sup>a</sup> All titrations made at 30° C.

<sup>b</sup> NaCN solution = 0.007728 gram of Ni per ml.

The end point obtained with the silver solution is sharp and suitable for deflection end points. In view of the data just presented, all the results in this investigation were obtained by using the cloud point (AgI formation) for the end point, as indicated by the photronic cell.

**SODIUM CYANIDE-SILVER NITRATE RATIO.** In sodium cyanide-silver nitrate titrations the question naturally arises as to what conditions must prevail when the relationship  $\text{Ni} = 2\text{Ag}$  holds. It was found that the sodium cyanide-silver nitrate ratio is affected by alkalinity, temperature, the presence of citrates, and the concentration of silver. However, under the conditions of the recommended procedure, the nickel equivalent of the standard silver nitrate solution can be taken as  $1\text{Ni} = 2\text{Ag}$ , since the amount of silver solution used in a determination is not enough to cause an appreciable error.

**EFFECT OF EXCESS AMMONIA CONCENTRATION.** Table I shows the results obtained by the recommended procedure when the amount of 7.5 *N* ammonia was varied from just alkaline to 25 ml. in excess. The consumption of cyanide decreases with an increase in alkalinity.

TABLE II. EFFECT OF TEMPERATURE ON THE REACTION BETWEEN NICKEL AND CYANIDE IONS

(1-gram samples of iron-nickel alloy, 29.96 per cent nickel)

Temperature of Solution ° C.	NaCN Added	AgNO <sub>3</sub> Used	Nickel <sup>a</sup> Found	Error
° C.	ml.	ml.	Gram	Mg.
10	39.92	8.3	0.2977	-1.9
	39.91	9.9	0.2961	-3.5
20	39.91	6.8	0.2992	-0.4
	39.88	7.0	0.2987	-0.9
30	39.88	6.3	<i>b</i>	...
	39.90	6.1	....	...
40	39.89	5.9	0.2999	+0.3
	39.91	5.9	0.3001	+0.5
50	39.88	5.0	0.3003	+0.7
	39.92	5.6	0.3004	+0.8

<sup>a</sup> An excess of 5 ml. of 7.5 *N* ammonia used in all titrations.

<sup>b</sup> NaCN solution = 0.007666 gram of Ni per ml.

**EFFECT OF TEMPERATURE.** Table II shows the results obtained by the recommended procedure when the tempera-

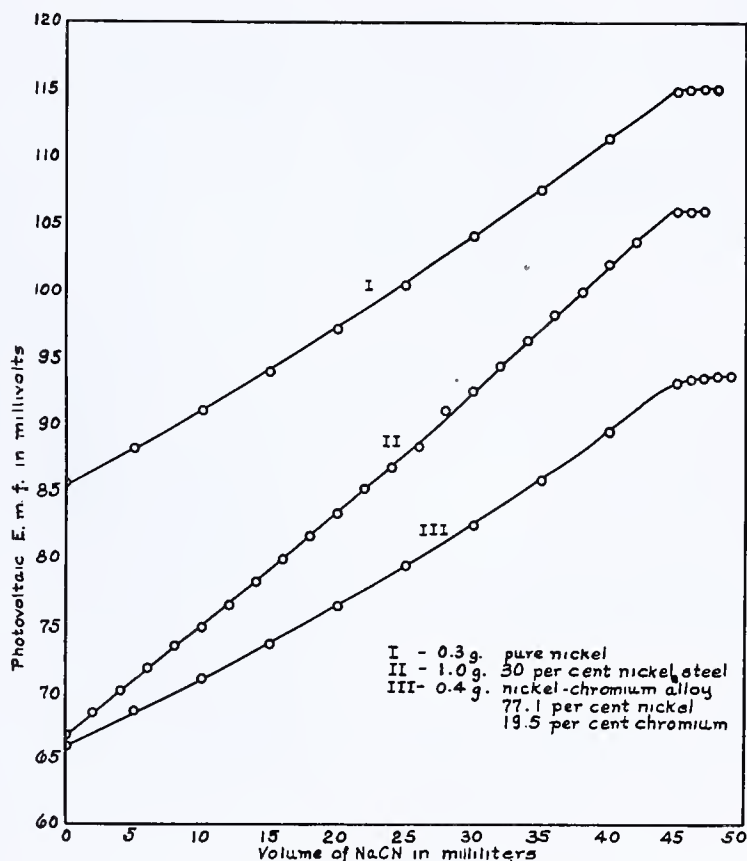


FIGURE 3. PHOTOMETRIC TITRATION OF  $\text{Ni}(\text{NH}_3)_6^{++}$  WITH NaCN

ture was varied from 10° to 50° C. The consumption of cyanide increases with an increase in temperature.

**EFFECT OF IRON AND NICKEL CONCENTRATION.** The data presented in Table III show that varying amounts of iron have only a slight effect on the reaction between nickel and cyanide ions. A nickel concentration of 0.05 to 0.4 gram per 500 ml. of solution does not affect the accuracy of the results obtained for nickel. It appears that the concentration of nickel could be considerably increased and still yield values which are correct to within 0.1 per cent.

TABLE III. EFFECT OF IRON AND NICKEL CONCENTRATION ON REACTION BETWEEN NICKEL AND CYANIDE IONS

Nickel <sup>a</sup> Alloy Taken	B. of S. <sup>a</sup> 55a Taken	Nickel Present	NaCN Added	AgNO <sub>3</sub> Used	Nickel <sup>b</sup> Found	Error
Gram	Gram	Gram	ml.	ml.	Gram	Mg.
1.0000	....	0.4134	48.95	7.1	<i>c</i>	...
1.0000	....	0.4134	49.00	6.5	....	...
0.8800	0.1200	0.3638	43.22	6.9	0.3639	+0.1
0.8800	....	0.3638	43.05	5.8	0.3636	-0.2
0.7300	0.2700	0.3018	35.97	7.0	0.3015	-0.3
0.7300	....	0.3018	36.57	11.5	0.3023	+0.5
0.5900	0.4100	0.2440	29.36	7.5	0.2443	+0.3
0.5900	....	0.2439	29.67	10.6	0.2440	+0.1
0.4400	0.5600	0.1820	21.79	4.9	0.1819	-0.1
0.4400	....	0.1819	22.29	9.2	0.1821	+0.2
0.2500	0.7500	0.1035	13.01	7.6	0.1037	+0.2
0.2500	....	0.1034	13.16	9.6	0.1033	-0.1
0.1200	0.8800	0.0498	6.58	6.2	0.0499	+0.1
0.1200	....	0.0496	6.77	8.6	0.0495	-0.1

<sup>a</sup> Nickel alloy contains 41.34% Ni, 0.07% Cu, and 0.02% Co. National Bureau of Standards open hearth iron 55a contains 0.019% Ni, 0.046% Cu, and 0.008% Co.

<sup>b</sup> Corrected for copper and cobalt present.

<sup>c</sup> NaCN solution = 0.008596 gram of Ni per ml., calculated from Ni + Co + (0.8 × Cu).

**EFFECT OF COPPER AND COBALT.** During melting operations, nickel limits must be held within a very small range to control the final magnetic properties of the alloy. By correcting for small amounts of copper and cobalt known to be present in the mix, it is possible to control the nickel content within a range of 0.2 per cent. The copper corrections in



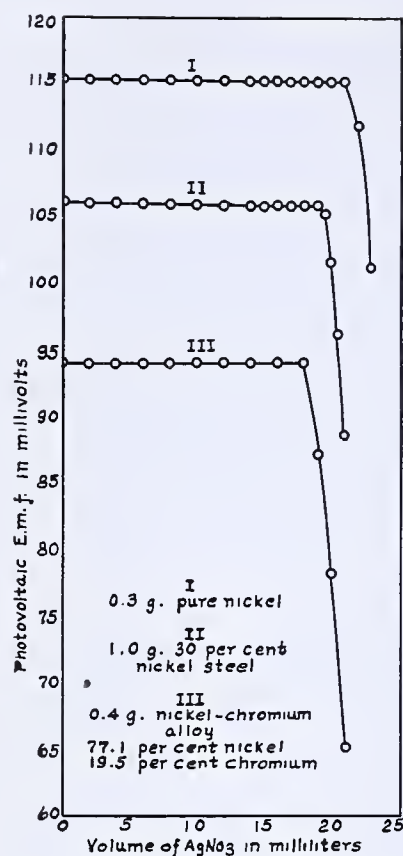


FIGURE 4. PHOTOMETRIC TITRATION OF EXCESS  $\text{CN}^-$  WITH  $\text{AgNO}_3$

Table IV were made by using the factor 0.807 to convert it to its nickel equivalent.

The theoretical relation of cobalt and cyanide is usually given as  $1\text{Co} = 5\text{CN}$ . In experiments where cobalt alone was titrated according to the recommended procedure, it behaved according to the indicated ratio. When 0.7 gram of iron was added, the reaction was suppressed to the extent that a relation of approximately  $1\text{Co} = 4\text{CN}$  was indicated. When large amounts of nickel, such as 0.3 gram, were added with the iron, the values for the nickel found showed good recoveries when corrected by using the relation of  $1\text{Co} = 4\text{CN}$ .

#### EFFECT OF CHROMIUM.

A solution of nickel sulfate was standardized by electrolytic deposition. An average of 0.3017 gram of nickel per 50 ml. of solution was obtained, including the small amount of nickel remaining after electrolysis. The chromium was added by using a c. p. grade of sodium dichromate. It was reduced to  $\text{Cr}^{\text{III}}$  with a small excess of sulfurous acid and boiled. The solution was treated with bromine water and again boiled to expel the excess bromine.

Large amounts of chromium are exceedingly hard to retain in ammoniacal solution, regardless of the amount of citric acid solution used. It was found that 0.3 gram of chromium could be held in solution with reasonable amounts of citrate if considerable ammonium chloride was also used. In the experiments shown in Table V, 25 grams of ammonium chloride were used in conjunction with the recommended procedure.

Both Johnson (3) and Peters (8) claim that the end point cannot be determined accurately unless the chromium is first oxidized to  $\text{Cr}^{\text{VI}}$ . With the phototitrimeter, a good end point is obtained regardless of the valence or amount of chromium, but when more than 0.1 gram of chromium is present, the nickel titer, as obtained on pure nickel, is slightly low. For high-chromium alloys, therefore, a weight of sample should be taken which does not contain more than 0.1 gram of chromium.

### Comparison of Results by Several Methods

**ELECTROLYTIC METHOD.** The 30 per cent nickel steel previously referred to was standardized electrolytically. The procedure used was as follows:

Accurately weighed 1-gram samples were dissolved in 500-ml. Kjeldahl flasks with diluted hydrochloric acid (1 to 1) and oxidized with nitric acid. The solutions were evaporated to low volume and double ether separations made to remove most of the iron. The acid layers were evaporated to fumes with sulfuric acid, cooled, and diluted with water. The solutions

were saturated with hydrogen sulfide to precipitate the copper, and filtered on small papers. The filtrates were boiled to expel hydrogen sulfide, oxidized with bromine, and again boiled to expel the excess bromine. The residual iron was twice precipitated with diluted ammonium hydroxide and the filtrates were evaporated to a volume of 150 ml. An excess of 35 ml. of ammonium hydroxide was added for the electrolysis. All determinations were corrected for the small amounts of nickel remaining after electrolysis.

An average of four determinations gave a value of 29.96 per cent nickel. The sample was found to contain 0.10 per cent copper. The cobalt was determined by using Hoffman's procedure (2) to separate the iron, nickel, etc. When 25-gram samples were used, less than 0.005 per cent of cobalt was indicated.

**CYANIDE TITRATION METHOD.** Three 1-gram samples of the 30 per cent nickel steel were analyzed for nickel by the recommended procedure. An average value of 29.96 per cent nickel was obtained. The cyanide solution was standardized on a synthetic mixture of 0.3000 gram of pure nickel and 0.7000 gram of National Bureau of Standards open hearth iron 55a.

**DIMETHYLGLYOXIME METHOD.** The procedure used for the dimethylglyoxime method was as follows:

Accurately weighed 1-gram samples were dissolved in 20 ml. of diluted nitric acid (1 to 1) and diluted to 1 liter in a calibrated flask. One hundred-milliliter portions (0.1-gram samples) were transferred to 400-ml. beakers using a calibrated pipet. Ten milliliters of hydrochloric acid and 20 ml. of citric acid solution were added, and the solution was diluted to about 200 ml. and neutralized with diluted ammonium hydroxide (1 to 1). Seven milliliters of glacial acetic acid were added and the solution was heated to boiling. Forty milliliters of dimethylglyoxime solution (10 grams of dimethylglyoxime and 9 grams of sodium hydroxide dissolved in 1000 ml. of water) were added, the solution was neutralized with diluted ammonium hydroxide (1 to 1), and then 5 ml. were added in excess. All solutions were then

TABLE IV. BEHAVIOR OF COPPER AND COBALT IN NICKEL TITRATIONS

(1-gram samples of iron-nickel alloy, 29.96 per cent nickel)					
Copper Added	Cobalt Added	NaCN Added	$\text{AgNO}_3$ Used	Nickel <sup>a</sup> Found	Error
Mg.	Mg.	Ml.	Ml.	Gram	Mg.
...	...	41.91	8.5	<sup>b</sup>	...
...	...	41.94	8.7	...	...
2.0	...	42.22	9.1	0.2997	+0.1
2.0	...	42.21	8.8	0.2999	+0.3
...	5.0	42.40	7.1	0.2996	±0.0
...	5.0	42.48	8.1	0.2992	-0.4
2.0	5.0	43.01	9.9	0.2997	+0.1
2.0	5.0	43.00	10.0	0.2995	-0.1

<sup>a</sup> Corrected for copper and cobalt added.

<sup>b</sup> NaCN solution = 0.007351 gram of Ni per ml.

TABLE V. EFFECT OF CHROMIUM ON REACTION BETWEEN NICKEL AND CYANIDE IONS

(50 ml. of $\text{NiSO}_4$ solution, equivalent to 0.3017 gram of nickel)				
Chromium Added ( $\text{Cr}^{\text{III}}$ )	NaCN Added	$\text{AgNO}_3$ Used	Nickel <sup>a</sup> Found	Error
Gram	Ml.	Ml.	Gram	Mg.
...	36.84	14.4	<sup>b</sup>	...
...	36.82	14.4	...	...
0.1	36.76	13.9	0.3016	-0.1
0.1	36.78	14.7	0.3010	-0.7
0.2	36.82	16.9	0.2991	-2.6
0.2	36.84	17.4	0.2988	-2.9
0.3	36.87	18.7	0.2978	-3.9
0.3	36.83	18.8	0.2973	-4.4

<sup>a</sup> Recommended procedure + 25 grams of  $\text{NH}_4\text{Cl}$ .

<sup>b</sup> NaCN solution = 0.008583 gram of Ni per ml.



allowed to digest for 30 minutes at about 75° C. The precipitates were collected in weighed platinum Gooch crucibles with asbestos beds, washed five to six times with hot (70° C.) distilled water, and dried at 110° C. for 1 hour. The factor 0.2032 was used to convert the weight of nickel dimethylglyoxime to nickel.

The average of five closely agreeing results gave a value of 29.82 per cent of nickel in the 30 per cent nickel steel.

When an alcoholic solution of the dimethylglyoxime was substituted for the sodium hydroxide solution in the method just described, an average of two determinations gave 29.70 per cent of nickel. According to Lundell, Hoffman, and Bright (5), alcohol has a greater solubility effect than ammonium hydroxide, ammonium salts, or alkali acetate.

The difference between the electrolytic and the dimethylglyoxime value is large compared to the close agreement obtained by the cyanide method based on pure nickel. The following experiments were made to determine whether the difference could be due entirely to the solubility of the nickel dimethylglyoxime.

One-gram samples of the 30 per cent nickel steel were dissolved in nitric acid, diluted to 1 liter, and divided into ten portions. The nickel in all ten portions was precipitated with dimethylglyoxime (sodium hydroxide reagent), filtered, washed, and run in all respects under the same conditions as the original dimethylglyoxime standardization. The precipitates were discarded and the filtrates evaporated to dryness. The citric acid, the excess reagent, and the ammonium salts were destroyed by oxidation with nitric and perchloric acids. The portions were combined and the remaining nickel was again precipitated in a small volume with dimethylglyoxime.

An average of two such runs gave a result of 0.12 per cent of nickel, to which 0.01 per cent should be added to allow for the final solubility. This corrected value ( $29.82 + 0.13 = 29.95$ ) is in very good agreement with both the electrolytic and the cyanide values.

A number of other cases seem worthy of reporting. A sample of Invar was found to contain 35.90 per cent of nickel by cyanide titration, based on pure nickel. The dimethylglyoxime method, using 0.1-gram samples (aliquoted from 1-gram samples), showed 35.62 per cent of nickel.

In another case, an iron-nickel alloy was found to contain 41.34 per cent of nickel by cyanide titration, based on pure nickel. The dimethylglyoxime method, using 0.08-gram samples (aliquoted from 1.6-gram samples), showed 40.99 per cent of nickel.

An alloy of the 80 per cent nickel-20 per cent chromium type was analyzed for nickel by cyanide titration, using accurately weighed 0.4-gram samples, the cyanide solution being standardized against pure nickel. An average of 77.2 per cent of nickel was found. An average of 77.1 per cent of nickel was found by standardizing against 1-gram portions of the 30 per cent nickel steel (29.96 per cent of nickel). The dimethylglyoxime method, using 0.04-gram samples (aliquoted from 0.4-gram samples), gave a value of 76.7 per cent of nickel.

A determination of nickel by the recommended procedure in National Bureau of Standards 18 Cr-8 Ni steel 101 gave an average value of 8.49 per cent of nickel, after correcting for copper and cobalt. (Cobalt is not listed on the certificate, but this laboratory obtained a value of 0.058 per cent. The certificate value for copper is 0.055 per cent.) The cyanide solution was standardized on a synthetic mixture of 0.2800 gram of the nickel steel (Ni = 29.96), 0.175 gram of chromium ( $\text{Cr}^{III}$ ), and 0.5 gram of National Bureau of Standards open hearth iron 55a. The certificate value of 8.44 per cent of nickel for this standard may be slightly low, since the dimethylglyoxime method was used by most of the coöperators listed on the certificate of analysis.

## Conclusions

A photometric apparatus has been developed to detect the end point in the cyanide titration method for nickel and found to be greatly superior to the eye, particularly in analyses of high-chromium alloys.

It is possible to run duplicate determinations in 35 to 40 minutes on iron-nickel alloys. High-chromium alloys necessarily require more time because of the difficulty of dissolving such samples. The accuracy that can be expected is of the order of 0.1 per cent.

The solubility of nickel dimethylglyoxime is demonstrated and it is shown that less dependence should be placed on this method when applied to high-nickel steels where the highest order of accuracy is desired.

## Acknowledgment

The author wishes to thank C. Sterling and W. A. Wesley of the International Nickel Company for the pure nickel used in this work. He wishes also to thank the officers of the Carpenter Steel Company for their encouragement during the progress of this work.

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## The Symbol Dz to Signify Dithizone

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CONSIDERABLE literature has accumulated in regard to use of diphenylthiocarbazone (phenylazothionormic acid phenylhydrazide) as an analytical reagent. Users of this substance soon contracted the name to dithizone, but so far as is known to the writer the only symbol proposed to represent the name is D. Since this symbol is now commonly used to designate deuterium, the heavy isotope of hydrogen, it should not be used to represent anything else.

The writer proposes the symbol Dz to represent dithizone. This will avoid confusion with anything else and will facilitate writing formulas or equations in which the radical dithizone occurs. When the word is used as the name of the reagent, diphenylthiocarbazone, it should be spelled out "dithizone."

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# A Precise Method for Sieving Analyses

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THE determination of the particle size distribution of a finely divided material by means of a sieving test is of considerable industrial importance in testing materials for conformity to specifications and in control over manufacturing processes. Specifications for a finished product usually call for the use of one or two sieves, with limits on the amount of oversize or fines or both. However, when the primary product of an industrial operation is a crystalline material with wide distribution of particle size which is to be separated subsequently into several grades according to particle size, a more complete sieving test is necessary for the intelligent design and control of large-scale separating equipment.

Sieving tests on commercial products, which are usually composed of irregularly shaped particles, are necessarily empirical and, in order to obtain reproducible results, all conditions of the tests must be rigidly standardized. But even under the best conditions, it is frequently impossible to obtain comparable results with two sets of sieves which are apparently identical, in spite of mechanical shaking and standardized time and sample size. In some cases, the retention of a product on two sieves which are nominally equivalent may vary by 20 per cent or more.

Work done under the sponsorship of the American Society for Testing Materials (1) has resulted in the standardization of sieve sizes in the "U. S. Standard" scale, and variations are held within rather wide limits by microscopic measurements of wire diameter and average number of wires per inch. In order to meet the A. S. T. M. specifications, a sieve must have average and maximum openings within the tolerances shown in Table I.

TABLE I. TOLERANCES ALLOWABLE UNDER A. S. T. M. SPECIFICATIONS

Sieve Nos.	Average Opening %	Maximum Opening %
4 to 18	3	10
20 to 45	5	25
50 to 120	6	40
140 to 200	8	60
230 to 325	8	90

Testing sieves having openings which fall within these tolerances are satisfactory for use on materials with a large average particle size, wide distribution of particle size, and regularly shaped particles. They become increasingly unsatisfactory, however, as the particle size distribution becomes narrower and as the particles become smaller and more irregular.

This objection has been recognized by several investigators at the Bureau of Standards, especially in sieving tests on cement (2, 4, 5). Wig and Pearson, after making a survey of the subject, concluded that an empirical sieving test on a standard sample was preferable to any other method of standardization that had been investigated. They recognized the connection between variation in the individual openings of the sieve and variations in sieving results, but found no satisfactory means of correlating them.

Sieving tests on finely divided materials other than cement have apparently received little or no attention from investigators. Many of these materials are being bought and sold on specifications, and in some cases they present considerable difficulty in that tests made by producer and consumer fail

to agree within wide limits. The work reported in this paper was done to sound out the possibilities of an absolute microscopic calibration of the testing sieves to be used on several specific products. It was desired particularly to avoid the use of standard samples, which is inconvenient and subject to cumulative errors, and which gives results that are empirical and of limited applicability.

## Microscopic Calibration of Sieves

All the new U. S. Standard testing sieves which were on hand in the laboratory were examined under a microscope in an extension mounting that permitted making measurements over the entire surface of the sieve. (A binocular microscope was used in the first observations, but was found to give erroneous results due to the angle at which the observations were made.) The microscope was equipped with a calibrated ocular micrometer, and combinations of scale and magnification were chosen so that a single opening of the sieve was equivalent to at least 15 scale divisions, except for those finer than about 60 microns, for which the number of scale divisions per opening, and hence the accuracy of measurement, was proportionately less. Measurements were made on representative groups of five adjacent individual openings along two diameters of the sieve, parallel to the warp and shoot, respectively, taking the same number of measurements in each direction. A total of 100 measurements was found to give calibrations reproducible within 1 per cent on sieves coarser than No. 200. Two hundred measurements give approximately the same accuracy on sieves No. 200 and finer. The average opening,  $\bar{X}$ , and the percentage standard deviation,  $d = 100\sigma/\bar{X}$ , for each sieve,  $\sigma$  being the standard deviation calculated by the method of grouping (3), are shown in columns 3 and 4 of Table II.

TABLE II. SIEVE CALIBRATIONS AND RESULTS OF TESTS

U. S. Standard No.	Nominal Opening Microns	$\bar{X}$	$d$	Sample A	Sample B	Sample C	Sample D	$X_1$	$X_2$
18	1000	1000	5.4	0.9	....	....	....	1000	1000
25	710	710	3.0	15.0	....	....	....	710	710
30	590	610	3.6	24.5	0.5	....	....	610	610
30	590	600	3.3	25.4	0.5	....	....	600	600
40	420	440	4.0	41.7	1.2	....	....	440	440
45	350	370	2.9	52.0	1.7	....	....	370	370
45	350	370	2.8	52.0	1.7	....	....	370	370
50	297	303	5.5	62.6	3.4	....	....	303	303
60	250	254	4.7	72.0	....	....	....	254	254
70	210	223 <sup>a</sup>	4.3	78.5	8.2	....	....	223	223
70	210	221	7.7	77.4 <sup>b</sup>	7.8 <sup>b</sup>	....	....	228	233
80	177	187	5.0	87.3	12.6	....	....	187	187
80	177	180	5.5	88.3	12.8	....	....	180	180
100	149	151	4.3	94.7	....	....	0.5	151	151
100	149	148	6.1	....	....	....	0.6	149	150
100	149	141	6.9	95.3	23.1	0.1	0.6	144	147
120	125	138 <sup>a</sup>	5.5	96.0	24.6	0.3	0.7	138	138
120	125	132	5.9	96.2	28.7	0.6	0.9	132	132
140	105	108	8.0	....	....	....	....	112	114
140	105	107	5.8	....	40.5	8.9	2.1	107	107
140	105	105	5.0	....	43.4	13.3	2.3	105	105
170	88	87	6.4	....	58.4	65.7	6.4	88	89
200	74	80 <sup>a</sup>	7.4	97.6	64.0	76.3 <sup>b</sup>	10.2	82	84
200	74	77	5.6	....	....	87.0	17.8	77	77
200	74	77	5.6	97.9	69.7	87.1	18.3	77	77
200	74	75	7.1	98.0	69.4 <sup>b</sup>	85.2 <sup>b</sup>	17.1 <sup>b</sup>	77	78
230 <sup>c</sup>	62	64	15.3	....	76.8	89.9	26.4 <sup>b</sup>	69	72
230	62	62	5.2	....	79.8	93.8	35.9	62	62
230 <sup>c</sup>	62	61	9.0	....	....	94.5	36.6	64	65
270 <sup>c</sup>	53	58 <sup>a</sup>	8.6	....	83.7	95.2	40.6	60	62
270 <sup>c</sup>	53	58 <sup>a</sup>	8.6	....	82.8	95.1	41.0	60	62
325 <sup>c</sup>	44	44	13	....	88.0	96.0	56.8	47	49
325 <sup>c</sup>	44	41	15	....	90.8	96.5	66.9	44	46

<sup>a</sup> Average opening outside A. S. T. M. specifications.

<sup>b</sup> Obviously out of line.

<sup>c</sup> Twill weave.

<sup>1</sup> Present address, Westvaco Chlorine Products, Inc., South Charleston, W. Va.



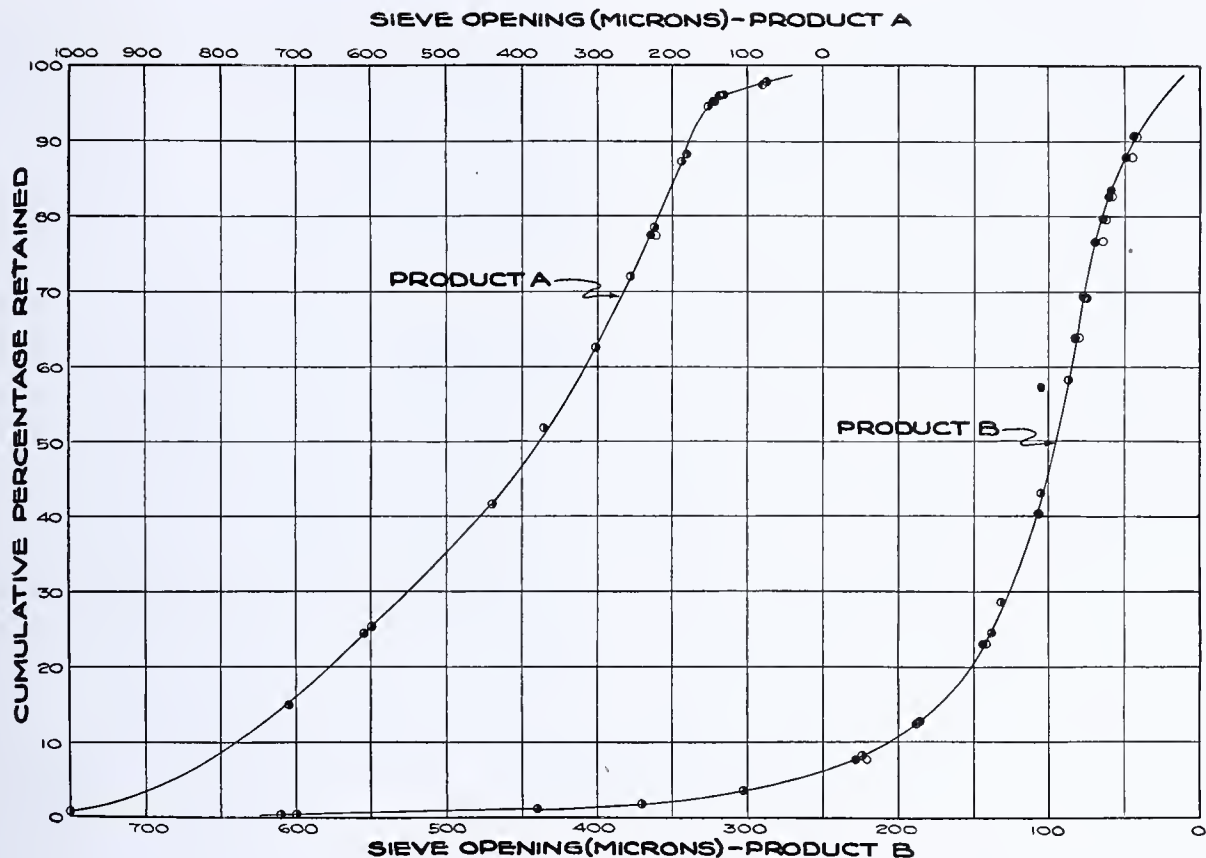


FIGURE 1

Nearly all the sieves had average openings which differed to some extent from their nominal openings. A few of the averages (as noted) fell outside the A. S. T. M. tolerances. But although no individual opening was found outside the specified tolerances, the uniformity as measured by the standard deviation varied greatly, and increased as the openings became smaller, as is to be expected from the increased difficulty of manufacture of fine sieves. In sieves for which the standard deviation is greater than 6 per cent, the nonuniformity is usually noticeable under casual inspection, especially in the spacing of the warp wires, which have more crimp and less accurate distribution.

Comparison of Test Results with Microscopic Calibrations

Since there is no known method of obtaining an absolute calibration of a sieve on material composed of irregularly shaped particles, the best means of judging the validity of the calibration of a set of sieves is the graphical representation of the results of sieving tests on standard samples. It must be assumed, of course, that the samples are representative of the types of material to be tested, and that the size distributions of their particles are smooth and continuous; but these assumptions appear to be justified. The materials chosen as standard test samples were commercial products with various physical characteristics, as follows:

- Sample A (dense soda ash)—wide size distribution, regular crystal shape
- Sample B (light soda ash)—smaller average size, more irregular particles
- Sample C (sodium bicarbonate, granular)—very closely sized, monoclinic prisms
- Sample D (sodium bicarbonate, powdered)—very small particles (many subsieve size), mixture of monoclinic prisms and fragments of crystals

The sieves were tested in groups of six, each group being selected to comprise a well-separated series covering as much of the range of particle size of the standard sample as possible; and in all tests the sieves were shaken mechanically by

a Tyler Ro-Tap sieving machine. Samples A and B were shaken for 3 minutes, samples C and D for 5. The results, reported as cumulative per cent retained on each sieve, are shown in columns 5 to 8 of Table II, and in Figures 1 and 2, in which the open and half-shaded circles represent retentions vs. average openings. The solid circles represent corrected values of several openings calculated by an empirical method described below.

The results furnish ample evidence of the futility of attempting to compare analyses made on two uncalibrated sieves, even though they may be of the same nominal size and in conformity with the A. S. T. M. specifications. The variations which may be expected in many instances are shown particularly well by the retention of samples C and D on the No. 200, 230, and 325 sieves.

If the average openings of the sieves are used in place of the nominal openings, the correlation is improved, but there still remains considerable irregularity in the sieving curves, especially in the finer sieve sizes. Those results which are most obviously out of line (Table II) are all on sieves which have a relatively large dispersion of the size of opening as indicated by the standard deviation of the measurements used to compute the averages. If the results on sieves having standard deviations greater than 6 per cent of the average are disregarded, the correlation of the remaining results is remarkably good.

The obvious solution to the problem of getting concordant sieving analyses is therefore to use only those sieves for which the standard deviation of the openings is no more than 6 per cent of the average. This would probably be a satisfactory solution for sieves with openings down to about 100 microns, but the mechanical difficulties involved in the production of finer sieves of the required degree of uniformity are so great that costs of inspection and rejection would be prohibitive. Some means of correcting either the average sieve opening or the results of tests on sieves with greater dispersion would be much more economical, at least until the technic of sieve manufacture is greatly improved.



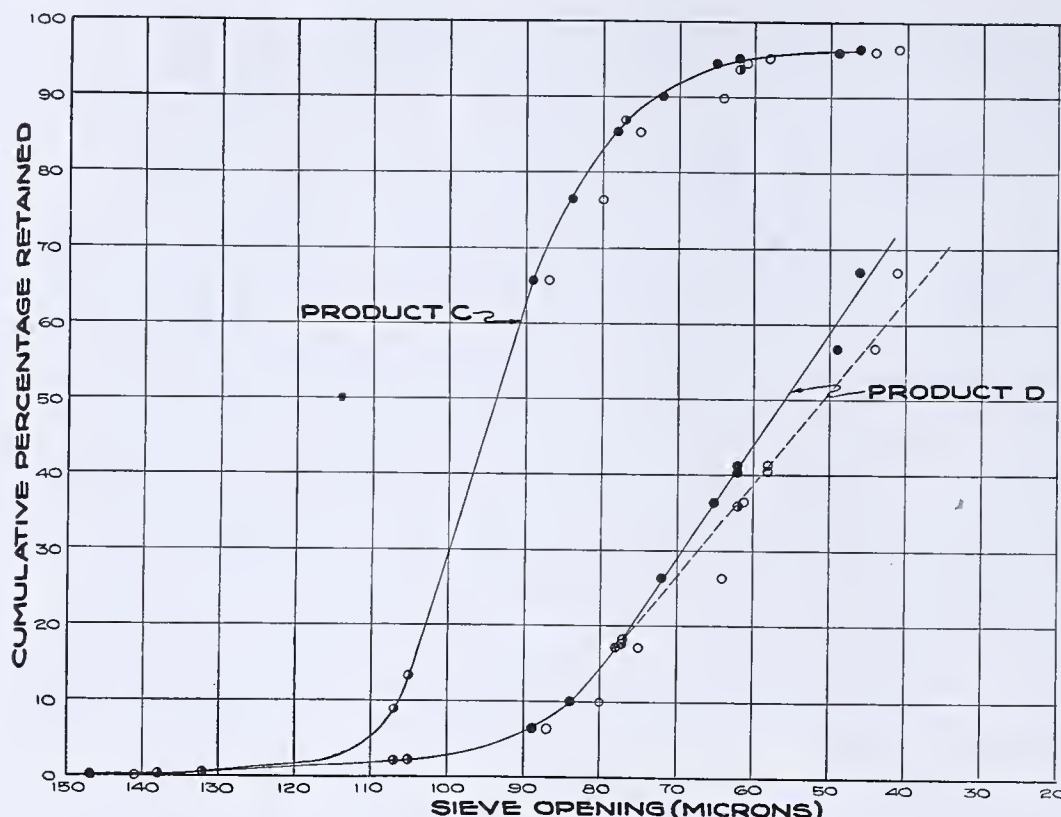


FIGURE 2

It was noted from the sieving curves that sieves with relatively large dispersion of size of opening always behave as if their average opening were somewhat larger than that calculated from the measurements. Also, the difference between the average opening of a sieve with high dispersion and that of a sieve having the same retention but a small dispersion increases as the standard deviation of the former increases above 6 per cent. This suggests that the erratic behavior is due to the relatively larger proportion of oversized openings which are sought out and passed through by slightly oversized particles shaken on sieves of high dispersion. If such is the case, then the error must be also a function of shaking time, for a relatively small number of oversized openings would have an increasing effect as the time of shaking is increased.

It is conceivable that a strictly theoretical treatment of the correction might be evolved for the ideal case in which the particles are perfect spheres with known size distribution, the openings perfect circles or squares, and the method of shaking produces a perfect random motion of all the particles over the entire surface of the sieve. But the difficulties of such an analysis are obvious, and since the practical utility of the results would be questionable, only an empirical treatment was attempted, which resulted in the following approximation, developed by trial and error:

$$X_t = \bar{X} \left[ 1 + 0.002t \left( \frac{d - 6}{0.06} \right)^{1/2} \right]$$

in which  $X_t$  is the effective opening for a shaking time of  $t$  minutes. When  $d$  is less than 6, making the correction term imaginary, the average opening is used without correction. There is no apparent theoretical justification for this, but since sieves with standard deviations no greater than 6 per cent of the average give results sufficiently concordant to be used without correction, and the method of correction gives good results for the other sieves, the method appears to be justified on pragmatic grounds.

The values for  $X_3$  and  $X_5$  calculated for the sieves used in this work are shown in columns 9 and 10 of Table II, and the

points representing the corrected values are represented on Figures 1 and 2 by the solid circles. The half-shaded circles represent sieves whose standard deviations are not more than 6 per cent of the average opening, and which therefore require no correction.

An inspection of the graphical data shows clearly why sieve calibrations based on empirical corrections determined by check tests on standard samples have not proved satisfactory—the correction to be added to the percentage retention depends not only on the sieve itself but on the slope of the sieving curve of the sample at the point in question. Thus, the correction on the 87-micron sieve is about 1 per cent for the finer sample and about 5 per cent for the coarser sample of the two shown in Figure 2. By applying the correction to the sieve opening, however, the sieve can be made to yield consistent results, as this correction is independent of the sample to be tested. It appears

also that the effective opening is independent of the nature of the material to be tested within certain limits, but the data do not cover sufficient ground to determine these limits.

TABLE III. CALIBRATION OF No. 230 SIEVES

Identification Mark	Weave	Average Opening Microns	Standard Deviation %	$X_3$ Calcd. Microns	$X_5$ Observed Microns
A	Twill	61	10.0	66	68.9
B	Twill	60	12.3	66	68.5
C	Plain	60	6.5	62	62.8
D	Twill	60	11.4	66	69.9
E <sup>a</sup>	Plain	59	10.4	64	61.9
F	Twill	62	8.5	66	71.9
G	Twill	60	9.5	65	71.0
H	Plain	61	6.1	62	61.2
I	Twill	59	11.1	64	69.3

<sup>a</sup> Old sieve with loose cloth.

The corrections add but little to the accuracy of the sieving curves of samples A and B because of their wide size distribution and regular particle shape. Sieve calibration is therefore unnecessary for tests of this type except to eliminate the possibility of the use of a sieve varying widely from the rated opening. However, the accuracy of the sieving curves of the closely sized and irregularly shaped particles of samples C and D is greatly increased when proper cognizance is taken of the calibrated openings and uniformity of the sieves. If sieves for use on products such as these are not calibrated and the nominal openings are used in determining the sieving curve, very grave errors may be obtained from sieves which are considerably off-size or nonuniform. All the sieves having standard deviations greater than 6 per cent gave direct results from 1 to 12 per cent lower than the correct point on the sieving curve, while the corrected sieve openings ( $X_3$ ,  $X_5$ ) gave results that lay on the curve, with the exception of the No. 325 sieves and one of the No. 230 on sample D.

Although the use of the correction improves the concordance of the results on these finer sieves, it was felt that further investigation was called for because the sieve which was most noticeably out of line after correction was the most uniform of all these finer sieves. For this purpose, a group of nine



No. 230 sieves was assembled, and each of them was calibrated and checked against a single standard sample on which results could be duplicated within 0.2 per cent. The data on this group of sieves are shown in Table III, and the results of the tests on the standard sample are plotted in Figure 3, where the open circles again represent average openings, uncorrected for dispersion, and the solid circles the corrected values. Data for other sieve sizes are included to establish the general form of the curve.

The average openings of the entire group of No. 230 sieves were in the range 59 to 62 microns; but in their behavior, the sieves were divided into two distinct groups. Those in the group of three, whose sieving characteristics fell in line with the other sieves in the series, were all made up with plain-weave cloth, which is standard for sieves No. 200 and coarser. The data on the two sieves with effective openings of 62 microns are considered more accurate than those on the third member of the group, not only because the corrections for dispersion were smaller, but because the third sieve was old and its cloth was loose. Those of the other group were made up with twilled cloth, which apparently behaves very differently; and since the correction formula is obviously inapplicable to this type of cloth, the "effective openings" as calculated by the correction formula are indicated as crosses, whose locations apparently have no physical significance.

In the light of these data the broken line shown on the curve for product D (Figure 2) appears to be a better approximation of the truth than the solid line which does not make allowances for the twilled sieves.

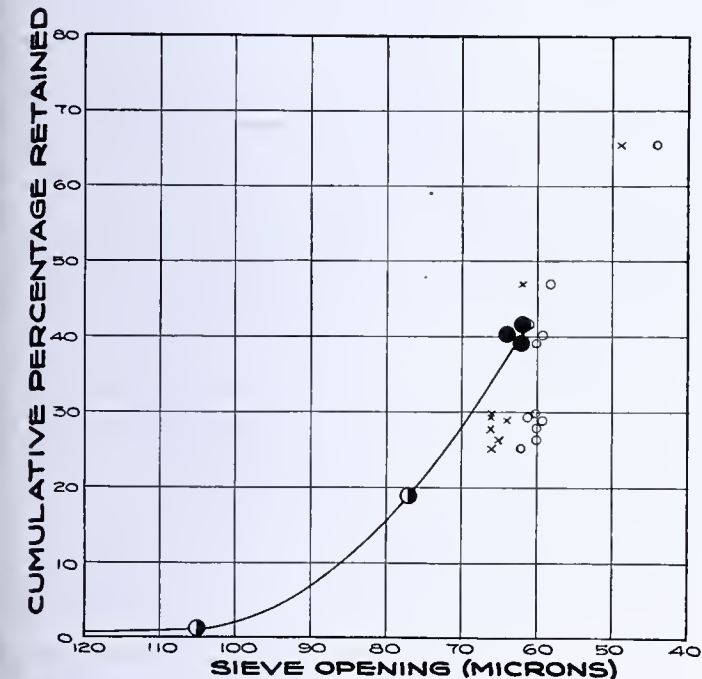


FIGURE 3

Two possible causes for the erratic behavior of the twilled cloth suggest themselves at once: (1) In the twilled cloth, only two of the four wires which bound each opening traverse the thickness of the cloth, the other two lying entirely on one side, one on the top and the other on the bottom; whereas all four wires of the plain-weave cloth traverse the cloth thickness at each opening. Hence, the distance between the projections of two adjacent wires on the plane of the cloth is somewhat less than the actual distance between them at the center line of the opening, and the effective opening is greater than that for a plain-weave cloth with the same horizontal spacing between the wires. (2) The axes of symmetry of the twill weave are not parallel to the wires, but at an angle of 45°, wherefore there is a tendency for the cloth to warp, throwing the warp and shoot wires out of their normal rectangular relation. This is noticeable in all of the twilled cloth ex-

amined, whereas the warp and shoot are usually at right angles in plain-weave cloth.

It would appear, therefore, that in any attempt to determine the effective opening of twilled cloth from its dimensions one must include correction factors for the ratio of wire diameter to average opening and for the angle between the warp and shoot wires. The determination of these factors would be rather involved, and would require either a large number of sieves or facilities for producing sieves in which these variables can be controlled.

It seems more practicable, therefore, to calibrate twill-weave sieves by comparison with calibrated plain-weave sieves in actual sieving tests. Unfortunately, however, such standards for comparison are not available at present. Sieves finer than No. 200 are produced only in twilled cloth, and the three plain-weave No. 230 sieves used for the work were found only with considerable difficulty. Two of the No. 230 plain-weave sieves have been preserved as standards, but none finer than this has been located.

Further refinement of the method of measurement will probably be required for calibration of the very fine sizes, such as the use of a filar micrometer and selection of microscope objectives of small aperture to increase the depth of focus, bringing the wires on opposite sides of the openings in twilled cloth into focus simultaneously.

### Influence of Method of Sieving

The technic (mode of sieving, sieve sizes, sample size, and time of sieving) for the test sieving must be standardized for each type and size of product.

Some form of mechanical sieve shaker must be used for reproducibility, economy of time, and convenience. The Tyler Ro-Tap used in this work gave very satisfactory results.

The sieve sizes must be selected to include the limits of the size distribution and enough intermediate sieves to give a well-defined curve. They must be selected far enough apart in mesh opening so that their full effect can be obtained within a short sieving time. Five properly selected sieves should be sufficient to determine accurately the size distribution curve of even a widely distributed product. The retention on any other standard sieve can be predicted accurately from the curve.

The sieving time required to obtain reproducible results decreases with sample size, but accuracy is lost in both sampling and weighing. The optimum size may best be fixed by determining the smallest sample that will give reproducible results. One hundred grams is a very convenient size, as the fractions are reported directly in percentages.

The influence of time of shaking is very important, being greatest when the particles are small and irregular. Enough time must be allowed for the fractions retained on the several sieves to approach constancy, but a protracted time only allows additional opportunity for the closely sized particles to seek out the openings slightly larger than average in each sieve. A balance between these effects can be obtained by sieving the same sample for time periods increasing in steps of one minute. The period after which the greatest sieve fraction begins to lose a constant amount for each succeeding minute is the optimum period on which to standardize.

### Summary

Testing sieves available on the market, even though they may conform to A. S. T. M. specifications, cannot be trusted to give accurate results without calibration. Methods of calibration by checking on standard samples are not generally satisfactory.



A method has been developed for determining microscopically the effective opening of plain-weave sieves and it has been shown that this value is independent of the size distribution of the material to be tested. This method corrects for both the deviation of the average opening from the nominal and the variations between the individual openings of a single sieve. There still remain discrepancies in the case of twill-weave sieves, wherefore these should be checked by comparison with calibrated plain-weave sieves if the accuracy of the results is of great importance.

Further work is needed to check the applicability of the method of calibration to sieves used on more varied materials and to improve the accuracy of the method. Such a program might well be undertaken in collaboration with sieve manufacturers.

### Acknowledgment

The authors are very grateful to William B. Kent for his valuable suggestions and criticism, and to the W. S. Tyler Company for the loan of some of the sieves used in this work.

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## Observations on the Rare Earths

### Quantitative Estimation of the Rare Earths by Means of Their Arc Spectra

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The determination of some individual rare earths in complex rare earth mixtures, by means of the Hilger EI quartz-type spectrograph using an internal standard, has been studied.

Magnesium, zirconium, and cerium oxides were tested as possible internal standards. Of these, zirconium oxide was found to be most suitable with respect to position and intensity of lines and rate of volatilization.

The region between 2500 and 3300 Å. was found to be the most suitable in number and intensity of lines and degree of dispersion.

The effects of other rare earths on the line intensities of an individual rare earth were found to be of similar magnitude, no matter which rare earth was added.

Duplicate standard plates for lanthanum, neodymium, samarium, gadolinium, dysprosium, ytterbium, and yttrium were prepared by photographing the arc spectrum of rare earth-zirconium mixtures of various ratios containing sufficient added lanthanum or neodymium oxides to keep the total rare earth content constant at all ratios.

The arc spectra of the rare earth oxides extracted from a number of typical rare earth ores with added zirconium oxide were photographed in a manner similar to that employed in preparing the standard plates.

The intensity ratios between the selected line pairs of rare earth and zirconium lines were determined on both the standard and the ore plates by means of a recording microphotometer. The percentages of the rare earths in the extracts of the ores were estimated by interpolating the ratios of the line pairs obtained from the ore plates on a logarithmic plot relating the intensity ratios and concentration of rare earths obtained from the standard plates.

The percentages of individual rare earths present in the ores were found to vary both with the type of ore and with its geographic origin.

The method was applied to the determination of the individual rare earths in an artificial mixture of rare earth oxides of known composition. The maximum error as calculated from the results was found to be  $\pm 15$  per cent.

THE selection of a suitable ore as the starting material for the preparation of a pure rare earth has always been attended by difficulty and uncertainty because of the lack of methods of analysis for the individual rare earths. This has been particularly unfortunate since, because of the lengthy and difficult processes of fractional crystallization and precipitation required to prepare a rare earth in a pure form, it is probably more important to choose as rich as possible a source in preparing the rare earths than in preparing any other elements. Early analysts, recognizing this, made such separations as were practicable and reported the rare earths in ores in percentages of cerium and yttrium groups and of cerium present. No very great advance in methods of analysis for



the rare earths was made until after the introduction of quantitative analysis by means of x-ray spectroscopy. This method has been employed by Goldschmidt and Thomassen, W. Noddack, I. Noddack, and K. Kimura to determine the percentages of individual rare earths present in ores, meteorites, and various artificial mixtures.

Another physical method of analysis which has come into wide use for the analysis of many elements is that employing arc spectra. This method, like that of x-ray spectroscopy, rests on the fact that, all other things being constant, the intensity of the spectrum line of an element is directly related to the amount of that element present in the sample. Many improvements over the dilution methods of Hartley, Leonard and Pollock, De Gramont, and other early spectrochemical analysts have been effected in the last few years. Gerlach was the first to introduce the idea of comparing the line intensities of the element to be determined with the intensities of the lines of another substance present in nearly constant amount from sample to sample. In this way the effects of such factors as exposure and development are eliminated, so that the relative intensities of the lines of the element being determined are more nearly a function of the concentration alone. The method of Gerlach has been modified by Nitchie and Standen, who introduce a definite amount of a selected substance not originally present to serve as the internal standard, and evaluate the relative line intensities photometrically. The method as developed by Nitchie and Standen is being widely used in the determination of a large number of metals in metallurgical products, minerals, biological fluids, etc.

The only application of this method to the determination of rare earths is the one made by Bauer, who quantitatively estimated lanthanum in a number of artificial mixtures containing calcium, aluminum, and iron using zirconium oxide as the internal standard.

In 1934 McCarty began a study to test the possibility of applying the method to the determination of the individual rare earths in complex rare earth mixtures such as are obtained on extraction of the ores.

### Individual Rare Earths in Complex Mixtures

About thirty typical rare earth ores, including gadolinites, monazites, euxenites, etc., were extracted by such suitable standard methods as Urbain's sulfuric acid extraction and Mueller and Meyer's pyrosulfate fusion method. The percentages of total rare earths present in the ores were calculated on the basis of weights of rare earth oxides obtained from known weights of representative samples of the ores.

Spectrochemical analysis by the method of Nitchie and Standen requires the addition of some substance not originally present to serve as an internal standard. For the analysis of the rare earths, McCarty chose magnesium oxide as the internal standard, since it gives lines of suitable intensity without giving many lines which would only further complicate the already rich spectra of the rare earths. Standard plates of the spectra of high-purity rare earth oxides (99.7 to 100 per cent pure) with magnesium oxide added were then prepared for cerium, lanthanum, praseodymium, neodymium, samarium, gadolinium, and yttrium. Oxides of the other rare earths having a sufficiently high purity were not available.

In making up a standard plate, quantities of a solution of the pure rare earth oxide in nitric acid were mixed with the proper amounts of a magnesium nitrate solution to give solutions having the following ratios of milligrams of rare earth oxides  $[(RE)_2O_3]$  to magnesium oxide: 10 to 1, 5 to 1, 4 to 1, 3 to 1, 2 to 1, 1 to 1, 0.5 to 1, 0.3 to 1, and 0.1 to 1. The spectra of these mixtures between the wave lengths 3400 and 6600 Å. were photographed. The instrument used throughout the entire investigation was a Hilger EI quartz-type spectrograph. All spectra were photographed on 25 × 10 cm. (10 × 4 inch) Cramer "spectrum proc-

ess" plates. The arc used to excite the spectra was generated between a pointed graphite anode and a graphite cathode containing a crater in which the 0.1-cc. samples of the solutions were placed and allowed to evaporate after a preliminary arcing for the purpose of focusing the arc on the slit of the spectrograph. Thirty-second exposures were made using an arc carrying 5.5 to 6 amperes and 220 volts drop across terminals. The plates were developed in a hydroquinone developer for 2.5 minutes, fixed for 20 minutes, and washed for 35 minutes, all at 12° C.

After the standard plates had been prepared, "line pairs" consisting of a rare earth line of suitable intensity and a magnesium line in fairly close proximity were selected and marked in the spectra at each concentration. The relative intensities of the lines in the line pairs were then determined photometrically. The microphotometer used in this investigation was one of standard design using a Ag-Bi thermocouple and recording the intensities as peaks on sensitized paper. A photometric tracing of the region containing the line pairs was made for each rare earth concentration on each of the standard plates. The ratios between the relative intensities of the rare earth and magnesium lines were then calculated by dividing the heights of the peaks corresponding to the magnesium lines in the line pairs. These ratios were calculated for the line pairs at each concentration and plotted as abscissas on double logarithmic paper against the rare earth concentrations plotted as ordinates. These plots resulted in very nearly straight lines which were used as standard curves relating intensity and concentration in the analysis of the rare earth mixtures obtained from the ores.

Half-gram samples of the rare earth oxides extracted from the ores were weighed out, dissolved in nitric acid, and so diluted with standard magnesium solution that a ratio of 10 mg. of rare earth oxide to 1 mg. of magnesium oxide was obtained. The spectra of these solutions were photographed maintaining all conditions of excitation, exposure, development, etc., as nearly as possible like those existing in the photography of the spectra of the standard plates. The rare earth on magnesium line pairs in the spectra were then photometered, the intensity ratios calculated from the heights of the corresponding photometric peaks, and the rare earth concentrations corresponding to these intensity ratios read off from the standard curves.

### Selection of Internal Standard

The values obtained by McCarty for the percentages of individual rare earths present in the ores had an estimated error of 10 per cent. It seemed desirable to determine whether these values could be checked when other line pairs were used and whether the accuracy of the method could be increased. Further study was therefore continued by Scribner. In searching for possible improvements, particular attention was directed at the selection of the internal standard. The advisability of using magnesium oxide seemed open to question, since magnesium oxide has a considerably lower boiling point than the rare earth oxides, and one of the criteria of a good internal standard is that it should volatilize at a rate similar to that of the substance to be determined. Zirconium, titanium, thorium, vanadium, and magnesium oxides were therefore studied by Scribner as possible internal standards for the determination of the rare earths. Zirconium oxide was found to be the most satisfactory, since it has a boiling point similar to the boiling points of the rare earth oxides, gives fairly strong lines at a low concentration, and furnishes a number of suitable lines in close proximity to suitable lines of the rare earths.

Standard plates for lanthanum, neodymium, samarium, yttrium, gadolinium, dysprosium, and ytterbium were prepared using a method similar to that used by McCarty except that zirconium oxide was substituted for magnesium oxide as the internal standard. The wave-length range photographed was that from 2500 to 3400 Å. Line pairs of the rare earths and zirconium were then selected, particular care being taken to select lines which were free from the influence of other rare earth and zirconium lines. The line pairs were photometered, the intensity ratios between rare earth and zirconium lines calculated, and the standard intensity ratio-concentration curves constructed, exactly as has been described above. Eight of the rare earth ore extracts prepared by McCarty were



analyzed, zirconium oxide being added as the internal standard. In other respects the method employed was essentially the same as that used by McCarty. The values obtained for the individual rare earth contents of the ores showed some rather large discrepancies from those obtained by McCarty and were never in very good agreement.

### Possible Sources of Error

The disagreement between the results of McCarty and Scribner indicated that further study of the problem was required. The investigation was therefore continued by Lorenz, special attention being given to possible reasons for discrepancies in the results and for possible sources of error. Among these the following seemed to be of particular importance: unsteadiness of the arc discharge, the difference in the rates of volatilization of the two internal standards used, the smallness of the dispersion of the instrument in the wavelength range used by McCarty with consequent overlapping of lines, the uncertainty of the position of the base line in the photometric tracings, and the influence of the other rare earths on the intensities of the lines of a particular rare earth in the spectra of the ores.

Attempts to steady the arc discharge between a pointed graphite anode and a graphite cathode impregnated with a rare earth salt solution, by varying the current and the diameter of the cathode and by withdrawing the hot vapors formed in the cathode by the application of suction to a hole bored through the anode, did not meet with success. It was found that the introduction of the rare earth salt solution into the unarced cathode, with subsequent drying in an oven, yielded a steadier arc than when the carbons were first arced and the solution introduced into the hot cathode was allowed to evaporate. This improvement was ascribed to the smaller porosity of the unarced carbon cathode which served to confine the rare earth material to the crater of the cathode instead of allowing it to permeate the walls of the crater and deposit on the sides of the cathode and there act as a point of discharge.

The influence of rare earths on the lines of other rare earths was studied by photographing the 10-mg. spectrum of a yttrium earth mixture, determining the relative intensities of yttrium, ytterbium, dysprosium, and gadolinium lines by means of the microphotometer, and calculating the intensity ratios between these lines. Ten-milligram samples of a lanthanum-cerium-praseodymium mixture and of a neodymium-samarium mixture were now added to separate 10-mg. samples of the yttrium earth mixture, the spectra photographed, the intensities of the same lines redetermined, and their intensity ratios again calculated. The intensity ratios of the lines in the yttrium mixture alone varied by 15 per cent or more from the intensity ratios of the lines in the yttrium earth mixture with added rare earths. The intensity ratios of the lines in the yttrium mixture with lanthanum-cerium-praseodymium added varied by about five per cent from the intensity ratios of the same lines in the mixture to which neodymium-samarium had been added. Similar tests with other mixtures gave comparable results and seemed to indicate that although a given rare earth line is visibly affected by the presence of another rare earth, the magnitude of this effect is the same no matter which of the rare earths is added.

The selection of the most suitable range for determinations with the Hilger EI spectrograph was studied. The region between 3300 and 4200 Å. was discarded because of the presence of carbon-oxygen and carbon-nitrogen bands, that above 4200 Å. because of the small dispersion of the instrument in that range, and that below 2500 Å. because of the scarcity of rare earth lines. The region between 2500 and 3300 Å. was found to be suitable both in the number of rare earth lines which occur and in the dispersion.

The ideal internal standard for the determination of a rare earth by means of the arc emission spectra should be another rare earth, since the rates of volatilization of the two would be very nearly equal. Since all rare earths are present in naturally occurring mixtures, however, before a rare earth could be used as the internal standard it was necessary to remove it completely from the mixture and then reintroduce it in definite amount. Cerium is the only rare earth which can be removed from a rare earth mixture with any degree of ease and its removal from a monazite extract by means of oxidation with alkaline permanganate was therefore carried out. At least four repetitions of the oxidation process were found necessary to effect a complete separation of the cerium and other rare earths. Cerium, moreover, gave too few lines of suitable intensity in the wave-length range 2500 to 3300 Å. at the concentration used for the internal standard. Zirconium oxide was therefore used as the internal standard.

Standard plates for lanthanum, neodymium, samarium, gadolinium, dysprosium, ytterbium, and yttrium were now prepared in the following way: Solutions of the high-purity oxide of these elements were dissolved in nitric acid and so diluted with a standard solution of zirconium oxide in nitric acid that the following ratios of milligrams of rare earth oxides to zirconium oxide were obtained: 5 to 1, 4 to 1, 3 to 1, 2 to 1, 1 to 1, 0.6 to 1, 0.5 to 1, 0.4 to 1, 0.3 to 1, 0.2 to 1, and 0.1 to 1. These values were also equal to the number of milligrams of rare earth oxide and zirconium oxide per 0.1-cc. samples of the solutions. The preliminary experiments had shown that the intensities of the lines of the rare earths are affected by the presence of other rare earths and since the individual rare earths were to be determined in the presence of rare earth mixtures in the ores some allowance for this effect had to be made. To compensate fully for this effect it would be necessary to add a rare earth mixture identical with that present in the ore to the standards. This, of course, is not practicable since it would necessitate a separate set of standard plates for each ore, even if the composition of the rare earth mixtures in the ores were known. Therefore, since the preliminary experiments had shown that each of the rare earths exercises nearly the same effect on the intensities of the lines of another rare earth, the problem was met by adding to each of the rare earth-zirconium mixtures used in making up the standard plates that quantity of another pure rare earth which would bring the total rare earth oxide concentration up to 10 mg. per 0.1 cc. Two standard plates, one containing lanthanum as the diluent and the other neodymium, were prepared for all rare earths listed except lanthanum and neodymium, for which only one standard plate each was prepared. The 0.1-cc. samples of the solutions of the standards were then measured into the craters of the cathodes and dried for 1.25 hours in an oven at 110° C. The spectra were photographed in the manner described above. The plates were developed for 4 minutes, fixed for 25 minutes, and washed for 30 minutes, all at 14° C.

Suitable line pairs of rare earth and zirconium lines were selected and photometered at each concentration. The base line of the photometric curve was determined by drawing a line through the points of maximum light transmittancy as recorded on the photometric tracing by allowing the plate light of the photometer to fall through a clear portion of the plate. The base lines were checked for correctness by calculating the ratio between the heights of peaks due to two zirconium lines and keeping this ratio constant for all succeeding determinations on the intensity ratio of the line pair. The intensity ratios of the line pairs were then plotted against the rare earth concentrations, as has already been described. The curves obtained by plotting the intensity ratios from two duplicate standard plates, one containing lanthanum as the diluent rare earth and the other neodymium, always lay very close together.

Twenty of the rare earth ores were then extracted, using the methods employed by McCarty. Particular attention was given to the complete removal of zirconium, since spectrographic traces of this element had been found in the extracts used by Scribner. The rare earth oxides so obtained were dissolved in nitric acid and diluted with zirconium oxide solution so as to give a rare earth oxide content of 10 mg. and a zirconium oxide content of 1 mg. per 0.1 cc. of solution. The arc spectrograms of the ores were made in triplicate following exactly the same procedure as that used in making the standard plates. The heights of the peaks corresponding to the lines of the line pairs, obtained on photometry of the spectra, were measured from a base line obtained as described under the photometry of the standard plates. The intensity ratios of the line pairs were calculated and the concentra-



tions of the rare earths determined from the standard curves. The results obtained did not agree with those of either McCarty or Scribner. The differences in the results obtained were undoubtedly due to such variations as the unequal dispersion at the wave length of the line pairs used in the various determinations, the choice of different internal standards, and the determination of the base line, as well as to the inevitable errors introduced by the inconstancy of the arc and the various factors which influence the intensity of the lines upon the plate.

In order to determine the accuracy which would be expected by the use of a standardized procedure, several control determinations were made upon artificial rare earth mixtures, prepared from materials of known composition. The individuals selected for this work were yttrium, neodymium, samarium, gadolinium, dysprosium, and ytterbium. These solutions were diluted with a standard zirconium solution and triplicate determinations were made according to the method employed in the analysis of the ores. The results are shown in Table I.

TABLE I. ARTIFICIAL MIXTURES

	Found				Present	Individual determi- nations	Error Av. com- pared with theoretical
	I	II	III	Av.			
	%	%	%	%	%	%	%
Y	35	38.5	42	38.5	40	17.5	- 3.75
Nd	22	22.5	22	22.17	20	2.5	+10.35
Sm	8	8	10	8.66	10	20.0	-13.4
Gd	8	9.5	8	8.5	10	15.0	-15.0
Dy	10	12	12	11.33	10	20.0	+13.3
Yb	12.5	10	11	11.17	10	25.0	+11.7
Net error +3.20							

While the net error in all determinations is not large, considering the difficulties which are inevitable, a glance at the fluctuations of individual determinations shows that the favorable net error is due to a series of compensating errors. The variations in the triplicate analyses are too large for a successful analytical method. But it must be borne in mind that there are no methods for complete analysis of rare earth ores and that the problem presents a good many serious difficulties. The authors' work has progressed far enough to convince them that these difficulties are not entirely insurmountable and that further refinements will develop a method by which the composition of the unfractionated extracts of rare earth ores may be made with a reasonable degree of accuracy.

Since this method of analysis depends upon the intensity of the lines in the arc spectra, it is evident that the length of exposure, the volatility of the internal standard, the dispersion of the spectroscope, the treatment of the plate, and the dependability of the microphotometer will all influence the accuracy of the method. It is believed that the precautions taken have largely eliminated most of these sources of error. The authors recognize that zirconia is not an ideal internal standard, but they believe that the major error is still to be found in the fluctuations of the arc during exposure. If it were possible to devise a method of producing a steady arc, they believe that this analytical process would be reasonably satisfactory.

One of the controversial points with respect to rare earth ores has to do with the percentage of the individual members of the group in various samples of the same ore. Do samples of monazite sand from various localities contain the same percentage of samarium? There have been decided differences of opinion in regard to the correct answer to such a question. If one is interested in the study of samarium, an accurate answer to the question is of prime importance. Some light can be thrown upon the composition of an ore by means of x-ray analysis, but evidently these methods have never been applied except to material after considerable fractionation. These attempts partially to separate the complex mixtures which are

obtained directly from rare earth ores are never quantitative and must always result in more or less serious disturbances of the quantities present. While the method of analysis by arc spectra is not yet ideal from the standpoint of accuracy, it is possible to get approximate results which are sufficiently refined to give some idea concerning the composition of some similar ores from varying localities.

The results obtained in the present study are tabulated in Table II. The values given are the average of two or more determinations of the intensity ratios obtained with the use of zirconium as an internal standard. The procedure was the same as was employed in making up the standard plates. A special effort was made to maintain uniform conditions of exposure, development, etc. Three arc spectrograms of each ore were taken to allow for inaccuracies resulting from the flickering of the arc. The selected line pairs were marked and photometered in exactly the same way as in the case of the standard plates. The base line was determined by the points of maximum light and checked for correctness by using the intensity ratios between zirconium lines determined in the standard plates. All photometric determinations were made in duplicate. The intensity ratios between the members of the various line pairs were calculated from the heights of the peaks representing zirconium and rare earth lines and the percentages corresponding to these intensity ratios read from the graphs made from the standard plates.

It was found that lanthanum could not be successfully determined in the yttrium earth ores because of the presence of several extremely strong yttrium lines a few angstrom units from the selected lanthanum and zirconium lines. Since no other suitable lanthanum line could be found, this element was not determined in the yttrium group ores.

TABLE II. COMPOSITION OF ORES

Ore	Source	Percentage Found						
		Y	Nd	Sm	Gd	Dy	Yb	La
Gadolinite	Arizona	32.25	5.5	3.5	4.95	2.6	5.0	...
	Probably European	36.00	2.0	2.15	3.0	2.0	5.0	...
	Hittero, Norway	23.25	7.4	3.6	3.45	2.90	6.0	...
Samarskite	Unknown	23.5	6.0	4.9	6.7	5.9	5.6	...
	American	23.25	6.2	5.1	4.82	6.2	1.17	...
	Mitchel Co., N. C.	21.8	6.8	4.9	4.2	6.4	1.5	...
Euxenite	Arendal, Norway	28.0	8.2	4.25	4.9	3.7	5.75	...
	Norway	29.0	7.4	4.55	4.1	3.3	6.05	...
Fergusonite	Norway	23.0	8.6	4.5	3.75	2.75	5.5	...
	Llano Co., Texas	25.0	7.4	3.3	3.4	2.4	6.2	...
	Arendal, Norway	28.4	10.25	4.0	4.1	3.85	5.85	...
	Ceylon	32.8	5.5	2.5	4.2	5.0	5.7	...
Cyrtolite	.....	28.7	5.5	2.5	4.2	5.0	5.7	...
Xenotime	.....	10.25	19.5	6.0	4.0	3.3	1.7	10.5
Tschefkinite	.....	2.0	18.0	4.5	2.6	1.0	1.0	4.55
Aeschynite	.....	24.25	7.4	2.95	3.3	2.15	7.1	...
Allanite	.....	7.0	22.5	6.0	3.75	2.0	1.02	...
Orthite	.....	20.5	13.25	4.8	3.6	2.45	2.95	...
Cerite	Bastnas, Sweden	2.0	20.00	4.25	1.75	1.0	1.0	9.9
Ampanga-beite	Madagascar	25.0	5.55	3.3	3.4	2.77	5.85	...

The results of these analyses must be accepted as tentative, but it is believed that they are sufficiently accurate to justify the conclusion that xenotime and allanite are better sources of neodymium than gadolinite would be. They also seem to indicate that similar rare earth ores from different localities show considerable variation in the percentages of the individual rare earths which they contain.



# Flow in Asphalts

## Shown by the Method of Successive Penetrations

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The method of successive penetrations proposed by Thelen and modified by Rhodes and Volkmann for the evaluation of flow properties has been applied to various kinds of asphalt. With most of the essentially viscous asphalts studied, the plot of the rate of shear versus shearing stress showed a negative intercept on the shearing stress axis; thus, the test as used is not a sound rheological method. Changes in technic were found to influence the rheological diagrams obtained with non-Newtonian but not with viscous asphalts. It was found that the flow was not laminar and that only a portion of the penetrated length of the needle was wetted by the liquid. Fundamental errors and difficulties, advantages, and precautions which must be observed are summarized.

IN RECENT years methods and apparatus have been developed by which the flow characteristics of materials of high consistency can be evaluated in absolute units; a review of the methods used with asphalts has been given (5). Since the apparatus required for such measurements is not available in most laboratories, the adaptation of equipment already in common use to the estimation of flow characteristics in absolute units should result in the more extensive use of rheological terms and methods.

Thelen (4) suggested that the penetrometer (1), an instrument universally used by bituminous technologists, could be utilized for evaluating the flow properties of asphalts and other materials of high consistency in absolute units. He proposed to do this by obtaining a series of successive penetrations without touching either the sample or needle. Rhodes and Volkmann (2) discussed the method critically, pointed out errors in Thelen's theory, and suggested that the test conditions could be compared with those prevailing in the falling coaxial cylinder viscometer. They also tested a viscous tar by the penetrometer method and their capillary tube viscometer (3); the results obtained by the two methods checked closely.

In the present paper the typical data obtained by applying the method of successive penetrations to viscous and non-viscous asphalts are reported, and conclusions are drawn concerning the merits of the test as a rheological method for the evaluation of flow characteristics.

### Description and Theory of Method

The sample is prepared and brought to temperature as described in the commonly used A. S. T. M. penetration test. The needle is brought into contact with the surface of the asphalt at a location close to the axis of the sample container. Since the sample frequently must be kept on the penetrometer table for some time, it should be surrounded during the test by a water bath maintained at the desired temperature (25° C., 77° F.).

Thelen describes the method as follows: "Without touching the needle or the sample, the needle is released for a series of successive time intervals and the resulting penetration noted after each interval. As the needle sinks deeper into the sample, the time intervals will have to be increased in order to get a measurable increment of penetration for the interval." Several measurements are thus obtained, with each successive one at a lower rate of shear and smaller shearing stress because, although the applied load remains constant throughout the series of tests, with each successive penetration the needle becomes embedded deeper in the asphalt.

Rhodes and Volkmann suggested that, if the above conditions are fulfilled, and if the resistance caused by friction between the blunt end of the needle and the asphalt is neglected, the test conditions might be comparable to those prevailing in the falling coaxial cylinder viscometer. This treatment is valid only if the needle does not approach too close to the bottom of the container. They also mentioned that the depression of the asphalt surface around the embedded needle may introduce an error because the theory assumes that the needle is wetted by the asphalt over the entire length recorded by the penetrometer.

The equation given by Rhodes and Volkmann for the calculation of viscosity can be expressed as follows:

$$\eta = \frac{M \times \Delta t \times 1.25 \times 10^7}{(P_f + P_i - 46)(P_f - P_i)} \quad (1)$$

where  $\eta$  = viscosity in poises

$P_f$  = final penetration in decimillimeters

$P_i$  = initial penetration in decimillimeters

$\Delta t$  = time interval in seconds

$M$  = mass in grams of the descending part of the penetrometer

From this equation the average shearing stress (at the surface of the needle) and the corresponding average rate of shear for any time interval  $\Delta t$  may be evaluated as follows:

$$\text{Shearing stress, } F = \frac{0.6243 M \times 10^6}{(P_f + P_i - 46)} \quad (2)$$

$$\text{Rate of shear, } \frac{dv}{dr} = \frac{0.0499(P_f - P_i)}{\Delta t} \quad (3)$$

The type of flow occurring in the asphalt should be determined from a plot of rate of shear,  $\frac{dv}{dr}$ , against shearing stress,  $F$ , provided Equation 1 is theoretically sound.

### Experimental Data

From determinations made on over one hundred different asphalts, the three following types of rheological diagram (rates of shear versus shearing stresses) have been obtained:

1. An occasional asphalt known, from measurements made in a rotating cylinder viscometer, to be essentially viscous gave a straight line which could be extrapolated through the origin. This case is illustrated by asphalt C which was produced from Trinidad petroleum by vacuum-steam distillation. The penetration at 25° C., 100 grams, 5 seconds, was 53, the ring and ball softening point was 120° F. (48.89° C.). Data obtained by the method of successive penetrations are given in Table I and Figure 1.

2. Most asphalts which were known to be essentially viscous liquids gave lines which, when extrapolated, indicated a negative yield value. Obviously, the slope of such a line is not a true

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measure of the viscosity of the asphalt. The data for asphalt A, also included in Table I and Figure 1, gives this type of diagram. Asphalt A with a penetration of 35 at 25° C., 100 grams, 5 seconds, and a ring and ball softening point of 122° F. (50° C.), was obtained from Californian petroleum by vacuum-steam distillation. Because the preponderance of the data obtained on viscous asphalts by the method of successive penetrations was of this character, any comparisons of the consistencies with those obtained on the same asphalts by means of absolute viscometers are of little value.

3. Asphalts known to be non-Newtonian liquids from measurements made in a rotating cylinder viscometer gave lines which could be extrapolated to intersect the shearing stress axis. In some cases curves were obtained which were concave to the shearing stress axis. The shape of the curve seems to be determined to a considerable extent by the rates of shear employed, which with the A. S. T. M. penetrometer are chiefly dependent upon the consistency of the material. With hard materials curved lines were usually obtained because high rates of shear could not be secured. The rate of shear-shearing stress plots at the higher rates attained with the softer non-Newtonian asphalts were in most cases straight lines. Venezuelan air-blown asphalt L (47 penetration at 25° C., 100 grams, 5 seconds, and 169° F., 76.11° C., ring and ball softening point), the data for which are recorded in Table I and Figure 1, illustrates one type of rheological diagram obtained for non-Newtonian asphalts by the method of successive penetrations.

Discussion of Method

The fact that rheology diagrams are frequently obtained with negative yield values shows that the method of successive penetrations as now used is not a sound rheological method. The probable sources of the difficulties encountered are the technic or procedure followed, and, to a greater extent, the theory which postulates laminar flow, as in the falling coaxial cylinder viscometer.

Numerous experiments have been conducted in an effort to determine the source of error in the method. Penetrations were made on samples of the same viscous asphalt using (1) the procedure described by Thelen, and (2) the same procedure except that the relaxation period between

TABLE I. FLOW DATA OBTAINED BY METHOD OF SUCCESSIVE PENETRATIONS

Total Time of Penetration	Total Penetration	Shearing Stress, F	Rate of Shear, dv/dr	Fluidity or Mobility
Sec.	Dm.	Dynes/sq. cm. × 10 <sup>-5</sup>	100/sec.	Rhes × 10 <sup>7</sup>
Asphalt C. Weight of moving part of penetrometer = 50 grams				
30	88 <sup>a</sup>	..	..	..
45	108	2.07	6.49	3.22
60	125	1.67	5.65	3.48
90	152	1.35	4.49	3.45
120	175	1.11	3.83	3.61
180	211	0.918	2.99	3.45
240	242	0.767	2.58	3.60
300	268	0.673	2.16	3.47
Asphalt A. <sup>b</sup> Weight of moving part of penetrometer = 100 grams				
5	35 <sup>a</sup>	..	..	..
15	61 <sup>a</sup>	..	..	..
25	79 <sup>a</sup>	..	..	..
35	93	4.95	7.14	1.37 <sup>c</sup>
45	106	4.07	6.49	1.50 <sup>c</sup>
55	118	3.51	5.69	1.51 <sup>c</sup>
65	128	3.13	5.14	1.52 <sup>c</sup>
85	146	2.74	4.52	1.51 <sup>c</sup>
105	162	2.39	3.94	1.49 <sup>c</sup>
125	176	2.14	3.57	1.49 <sup>c</sup>
145	190	1.96	3.42	1.55 <sup>c</sup>
165	202	1.81	3.12	1.51 <sup>c</sup>
185	214	1.68	2.92	1.51 <sup>c</sup>
205	225	1.59	2.72	1.48 <sup>c</sup>
Asphalt L. <sup>d</sup> Weight of moving part of penetrometer = 200 grams				
5	70 <sup>a</sup>	..	..	..
10	82	11.80	12.00	1.64
20	95	9.53	6.49	1.28
30	104	8.14	4.74	1.29
45	115	7.20	3.49	1.27
60	123	6.50	2.66	1.30
90	136 <sup>e</sup>	5.86	2.16	..
120	146 <sup>e</sup>	5.29	1.66	..
180	160 <sup>e</sup>	4.79	1.21	..
300	181 <sup>e</sup>	4.23	0.853	..
600	210 <sup>e</sup>	3.62	0.483	..

<sup>a</sup> These determinations are discarded because of the error introduced by the conical tip of the needle.  
<sup>b</sup> Average yield stress,  $F_0 = -25,000$  dynes per sq. cm.  
<sup>c</sup> These values are fictitious because of the negative yield stress.  
<sup>d</sup> Average yield stress,  $F_0 = 445,000$  dynes per sq. cm.  
<sup>e</sup> These experimental values are located in the curved region of the rate of shear-shearing stress plot and thus were not used to calculate the yield stress or mobility of the asphalt.

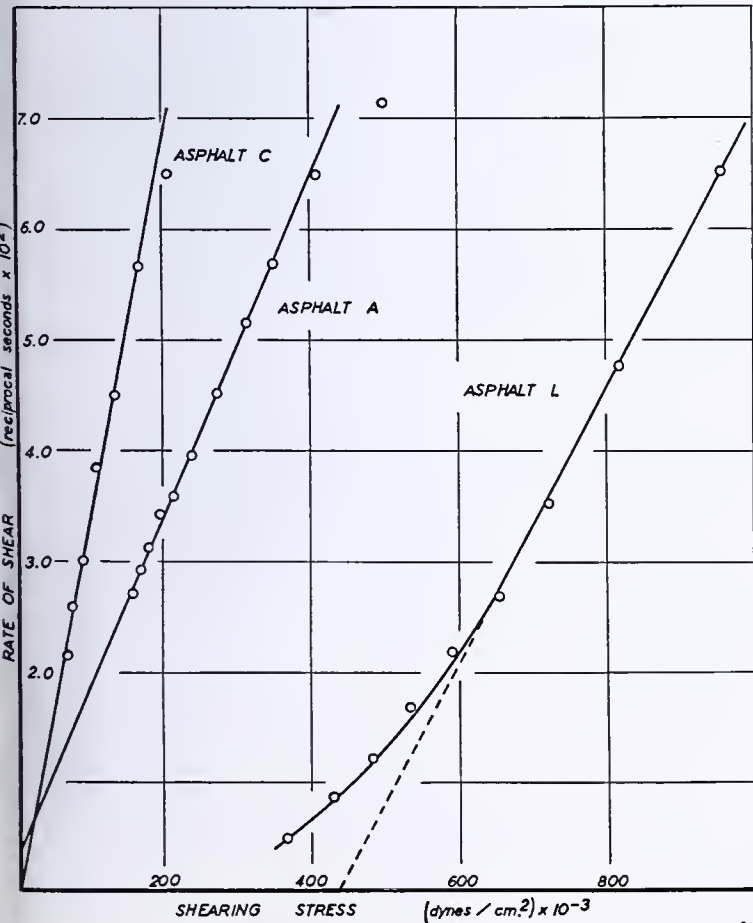


FIGURE 1. EXPERIMENTAL DATA

successive penetrations was increased six- to tenfold. Identical rheological diagrams were obtained by the two methods. This was also true when the results of a few penetrations of long duration were compared with those obtained by a larger number of penetrations of short duration. Thus, for the essentially viscous asphalts these modifications of technic have little effect on the results obtained.

When an air-blown asphalt (known to be distinctly non-Newtonian) was subjected to the two procedures described above, different rheology diagrams were obtained with each. This phenomenon occurs also in absolute viscometers because the data obtained for highly elastic, nonviscous materials are influenced by the rate of shear and procedure followed. Consequently, for the nonviscous materials any modifications of procedure may have a definite influence on the results obtained.

As mentioned above, Rhodes and Volkmann commented on the effect of the depression around the needle. This hollow is large enough to be seen by the unaided eye. However, with an opaque material like asphalt, a record of its depth and shape is very difficult to obtain. To acquire some direct evidence concerning the length of the penetrated needle wetted by the liquid material, a transparent Bakelite resin was placed in a square glass cell about 4.5 cm. on a side. The viscosity of this resin at 25° C. was 69,000 poises. The material was tested at about 25° C. with the A. S. T. M. penetrometer and the progress of the needle into the material photographed. Figure 2 shows the extent and shape of the surface created by the penetration of the needle. Using a cathetometer to measure the wetted portion of the needle, it was found that this varied from 79 to 82 per cent of the



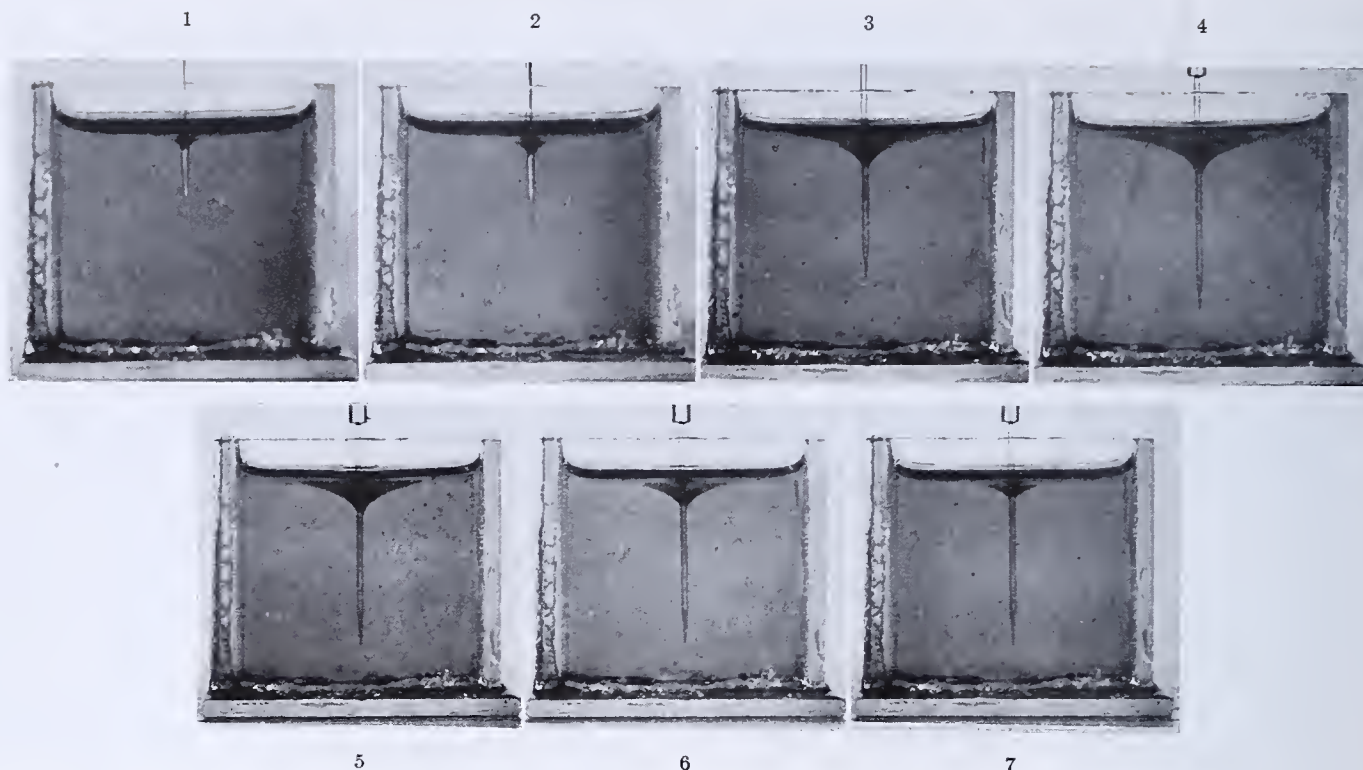


FIGURE 2. PENETROMETER NEEDLE ENTERING A BAKELITE RESIN POSSESSING VISCOSITY OF 69,000 POISES AT 25° C.

- 1, 2, 3. Entering
  4. Completion of penetration
  - 5, 6. Receding cone
  7. Receding cone, 5 minutes after 4
- 5, 6, and 7 show flow of resin into conical depression caused by penetration of needle

penetration recorded by the instrument. With material as fluid as this resin the depression around the needle is rapidly filled after the movement of the needle has been stopped.

From experiments made on a sample of resin containing air bubbles it appeared that the flow occurring in a sample of viscous material while being penetrated by a needle is not laminar, as has been assumed in the development of this test. Moreover, the flow appears to be so complex that it will be difficult to develop a theoretical treatment simple enough to be useful.

From a practical point of view the method has some value, although in its present form it should not be classed as a sound rheological method. Although the results are not accurate, complex liquids—e. g., air-blown asphalts—can be investigated over a range of rates of shear not easily studied in the absolute viscometers now available.

The consistencies of all asphalts increase with time; the rate and extent of age-hardening of any asphalt vary with its source and method of processing. Studies (6, 7) made with the falling coaxial cylinder viscometer have shown that the consistency increases at first because of the development of a reversible (thixotropic) structure which is complicated later by the appearance of permanent hardening.

Since the method of successive penetrations subjects the asphalt to higher rates of shear and shearing stresses than does the above-mentioned viscometer, it was thought that the unstable reversible portion of the time-hardening phenomenon might not be detected by the penetration method. A number of different asphalts have been investigated by the method of successive penetrations. The consistencies were found to increase with time at the higher rates of shear just as with the viscometers in which the rates of shear were much lower. Thus, the method seems to be useful in studies which require that a large number of samples be set aside for long periods of time in the containers in which they will later be tested.

Although there are several fundamental difficulties inherent in the method as now used and some precautions which must be observed, the method does offer certain practical advantages over absolute viscometers.

### Fundamental Errors and Difficulties

The method as described cannot be applied successfully to either very hard or very soft materials.

Visual evidence has been obtained indicating that the flow occurring in the sample is not laminar but is very complex.

For most essentially viscous asphalts the method has been found to give rheological diagrams indicating negative yield stresses. This shows that the test as now used is not on a sound theoretical basis.

### Precautions

Temperature must be regulated very carefully. The sample is on the penetrometer for some time and thus arrangements must be made for temperature control.

The penetrometer needle must be straight and uniform in cross section. It has been found that one-third to one-fourth of the needles purchased fail to comply with this requirement.

The needle must not approach too close to the bottom of the container.

### Advantages

The penetrometer is widely available; no special apparatus is required.

Time required for obtaining data at a number of different rates of shear is less than that required by the usual type of viscometer.

The container for the sample is a penetration tin which



is inexpensive and thus can be thrown away, eliminating the expense of cleaning. Such receptacles can be used in great numbers without incurring a large expense.

The method is of some interest for the evaluation of the flow properties of complex liquids and plastics at high rates of shear, and in the study of age-hardening of asphalts.

Acknowledgment

The authors are indebted to C. U. Pittman for helpful advice and criticism, and to O. R. Douthett for the photographs.

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Cerate Oxidimetry

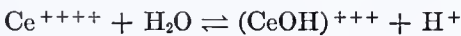
Theoretical Considerations and Determination of Approximate Electrode Reference Potentials

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THE use of solutions of cerium salts in volumetric oxidation reactions has been developed to its present extensive series (1) of practical applications mainly through the studies of H. H. Willard, N. H. Furman, and collaborators. The procedures up to the present are all carried out in a sulfuric or hydrochloric acid medium, using either ceric sulfate or its double salt with ammonium sulfate as the titrating solution. These methods have been classified under the general heading of ceric oxidimetry. The ceric ion has been assumed to be converted into the cerous ion upon reduction and the potential attained at standard state using ceric sulfate, cerous sulfate, and sulfuric acid as reactants has been shown by Kunz (4) to be 1.44 volts. The single-electrode potential in nitric acid solution has been recently determined by Noyes and Garner (6). The single-electrode potential in perchloric and hydrochloric acid solution has not been accurately determined.

The single-electrode potential found using cerium from the electrolytic oxidation of nitric acid solutions of cerous nitrate has been shown (6) to be 1.61 volts, a high value thought to be due to the fact that ceric nitrate in nitric acid solution dissociates normally, forming ceric and nitrate ions only. The lower oxidation potential obtained using ceric sulfate

in sulfuric acid solution—namely, 1.44 volts—was postulated to be due to hydrolysis of the ceric ion to form the complex ion  $(CeOH)^{+++}$ , according to the reaction:



If this explanation is correct, the oxidation potential of ceric sulfate should be increased by addition of sulfuric acid; this is not the case, as indicated by Willard and Furman (10). Furthermore, the higher potential of the ceric-cerous nitrate system in nitric acid solution should not be lowered appreciably by the addition of sulfuric acid; that the oxidation potential under these conditions is drastically decreased can be easily demonstrated by experiment.

This paper has for its objective the clarification of anomalies in the present theoretical concepts involved in the use of cerium in oxidimetry and the proposal of new concepts which can be shown more closely to harmonize theory with experiment.

Determination of Approximate Electrode Potentials

Cerous chloride, sulfate, nitrate, and perchlorate free from impurities were prepared, starting with the conversion of thorium-free ceric oxide of 40 per cent purity, forming chemically pure ammonium hexanitrate cerate,  $(NH_4)_2Ce(NO_3)_6$ , using the method previously described by Smith, Sullivan, and Frank (8). Cerous chloride was prepared from the complex nitrate by addition of excess hydrochloric acid and digestion to oxidize ammonia and decompose the nitrate radical. Cerous sulfate, nitrate, or perchlorate was then formed from the cerous chloride by evaporation with excess of the appropriate acid. These cerous solutions were converted to the corresponding ceric salts by anodic oxidation as described by Hengstenberger (2) in a diaphragm cell, using platinum electrodes. The resulting solutions were then analyzed to determine the exact degree of oxidation and their free acid content. In general, complete oxidation was shown to have resulted, or in case 1 or 2 per cent of cerium were left unoxidized appropriate correction was made in the subsequent determination of the ratio of oxidized to reduced cerium in the single-electrode potential studies. Solutions from 1 N to 8 N in free acid were then prepared. (Only 1 N hydrochloric acid solutions were studied.)

The single-electrode potential in each case was determined by reducing a known volume of solution by the addition of a few drops of 100 volume hydrogen peroxide, determining the exact

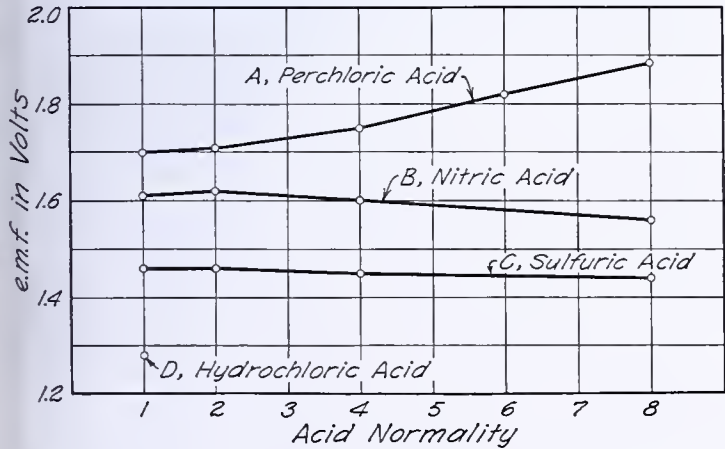


FIGURE 1. INFLUENCE OF ACID CONCENTRATION ON SINGLE-ELECTRODE POTENTIAL



point of complete reduction potentiometrically. The proper quantity of the same ceric solution was then added to produce a ratio of 1 to 1 reduced and oxidized cerium in the solutions of known free acid content. In the hydrochloric and sulfuric acid solutions, the saturated calomel electrode was used as reference with platinum as the other electrode. In the nitric and perchloric acid solutions, a saturated sodium nitrate or sodium perchlorate salt bridge was interposed between the saturated calomel electrode and the cell liquid to establish the 1 to 1 ratio of oxidized and reduced cerium, and the salt bridge was removed for reading the adjusted solution potential. This was done to prevent error from diffusion of chloride into the cell which is easily oxidized in the case of the nitric and perchloric acid solution of the tetravalent cerium. The final reading in direct contact with the saturated calomel cell was taken because of the unknown liquid junction potential from the salt bridge. Details of the potentiometer circuit are omitted, since an accuracy of greater than 0.01 volt is not claimed for these measurements.

TABLE I. SINGLE-ELECTRODE POTENTIAL VALUES

Acid Concentration <i>N</i>	Electrode Potentials with Reference to Normal Hydrogen Electrode			
	HClO <sub>4</sub>	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
1	1.70	1.61	1.44	1.28
2	1.71	1.62	1.44	..
4	1.75	1.61	1.43	..
6	1.82	..	..	..
8	1.87	1.56	1.42	..

The results are shown in Table I. The values for the nitric and sulfuric acid solutions are in agreement with those given by Noyes and Garner (6) and by Kunz (4) for normal concentration of acid. The remaining values were determined with equal care. The data of Table I are shown graphically in Figure 1. The concentration of tetravalent and trivalent cerium was 0.025 *N*.

Figure 1 and Table I show that the electrode potentials vary to a marked degree in solution of normal acid concentration. The single-electrode potential increases materially from its lowest value in hydrochloric acid on through sulfuric and nitric acid, to the highest value in the case of the perchloric acid solution. Following the assumption of a simple ceric-cerous ion relationship, the single-electrode potential should not be materially affected by change in acid concentration. This is not the case, since in both sulfuric and nitric acid the potential is lowered as the concentration of acid increases in

the range 4 to 8 *N*. The most marked change, that in perchloric acid solution, on the contrary, is an increase in potential with each increase in acid concentration.

Before a theoretical interpretation of the results obtained is proposed, the experimental titration data will be presented for the oxidation of ferrous iron using various strengths of hydrochloric, sulfuric, nitric, and perchloric acids, and the corresponding electrolytically oxidized cerium solutions in the same concentration of acids.

### Potentiometric Titrations

**FERROUS IRON BY CERIC CERUM.** Ferrous perchlorate was prepared by the solution of pure iron in perchloric acid, and was purified to eliminate a small amount of chloride by recrystallization from water. Ferrous nitrate was prepared from ferrous perchlorate by addition of the theoretical quantity of potassium nitrate and filtration, keeping the volume of the solution low and ice-cold. Ferrous sulfate was the usual stock reagent and ferrous chloride was prepared by reduction, using a Walden silver reductor (9). The ferrous solutions were adjusted to approximately 0.05 *N* strength in the normal concentration of the corresponding acids. The hydrochloric and sulfuric acid solutions of ferrous iron were titrated with approximately 0.05 *N* solutions of the ceric solutions in 1 *N* sulfuric hydrochloric acids, prepared as previously described. The nitric and perchloric acid solutions, 1 *N* in acid and approximately 0.05 *N* in ferrous nitrate and perchlorate, were similarly titrated using ceric solutions which were approximately 0.05 *N* in oxidizing value and 1 *N* in the corresponding acids. In the latter cases the potentiometric titration was carried out using a platinum electrode and the saturated calomel electrode but with a saturated sodium nitrate or sodium perchlorate salt bridge. The potentials were corrected for the salt bridge contact potential by eliminating the salt bridge at the completion of the titration, and the change in potential was noted.

The results are shown graphically in Figure 2. The potentials are given as the ordinates calculated to the basis of the normal hydrogen electrode. Curves A, B, C, and D are, respectively, those for the perchloric, nitric, sulfuric, and hydrochloric solutions. In each curve the value for the single-electrode potential of the normal ferrous-ferric system is the first point plotted at the left end of the curve and corresponds to a ferric-ferrous ratio of 1 to 1. The last point on each curve to the right corresponds to the single-electrode potential for the various systems at which the ratio of tetravalent to trivalent cerium is 1 to 1.

In Figure 2 the accuracy attained is shown by comparing the potentials obtained in curve A for the ferric perchlorate-ferrous perchlorate system recently determined (7), and the potentials obtained in curves B and C for the condition of equal concentrations of tetravalent and trivalent cerium which correspond to the values given by Noyes and Garner (6) and by Kunz (4). Values for the hydrochloric acid system cannot be cited. Only in the case of the perchloric acid solution is the value for the single-electrode potential of the ferric-ferrous system in agreement with the standard value. In all the remaining cases—those in nitric, sulfuric, and hydrochloric acid solutions—the observed value is lower than that given in tables of electrode potentials. The potential break at the equivalence point is greatest for perchloric acid solution, 650 millivolts for each 0.1 ml. of 0.05 *N* titrating solution. The corresponding values for the nitric, sulfuric, and hydrochloric acid solutions are, respectively, 425, 275, and 250 millivolts. At the end of the perchlorate and nitrate titrations the addition of 5 to 10 ml. of concentrated sulfuric acid instantly lowered the potential nearly to the much lower values obtained for the sulfuric acid titrations described later.

**FERROUS PERCHLORATE AT INCREASING CONCENTRATION OF PERCHLORIC ACID.** Ferrous perchlorate solutions in 1, 2, 4, 6, and 8 *N* perchloric acid were titrated using solutions of approximately 0.05 *N* tetravalent cerium in the corresponding concentrations of perchloric acid. The solutions were prepared and the titration performed under the same condi-

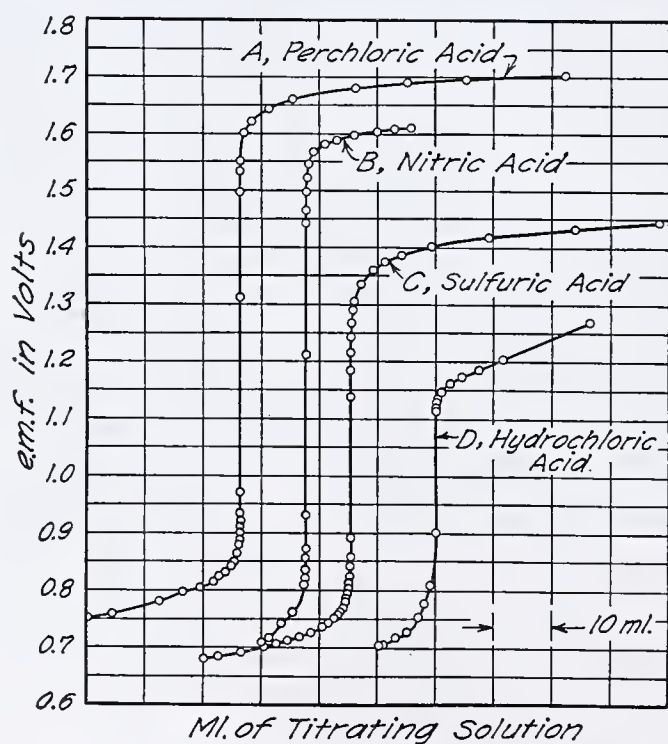


FIGURE 2. POTENTIOMETRIC TITRATION OF FERROUS IRON IN NORMAL PERCHLORIC, SULFURIC, NITRIC, AND HYDROCHLORIC ACIDS



tions as previously described. The data are shown graphically in Figure 3. The values for the single-electrode potential of the ferric-ferrous system increase with increase in normality of perchloric acid from the normal value of approximately 0.75 volt to approximately 0.88 volt at 8 *N* perchloric acid strength. The values at the points corresponding to equal concentrations of tetravalent and trivalent cerium correspond well with those given in Table I, which were determined in the absence of iron as previously described. At the end of each titration the addition of 5 to 10 ml. of concentrated sulfuric acid instantly lowered the potential nearly to the much lower values obtained for the sulfuric acid titrations described below.

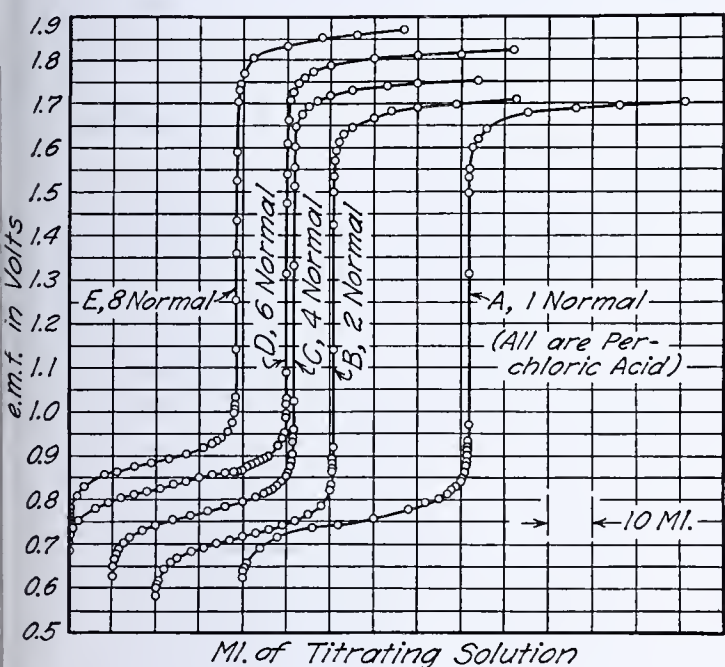


FIGURE 3. TITRATION OF FERROUS PERCHLORATE AT 1 TO 8 *N* PERCHLORIC ACID STRENGTH

FERROUS SULFATE AT INCREASING CONCENTRATION OF SULFURIC ACID. Weights of pure ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) corresponding to approximately 50 ml. of 0.05 *N* solutions were dissolved in the various concentrations of sulfuric acid and titrated, using approximately 0.05 *N* solutions of 100 per cent cerium in the tetravalent state in the same varying concentrations of sulfuric acid. The data are graphically shown in Figure 4.

The ferric-ferrous single-electrode potential is approximately 0.675 volt over the entire acid range of 1 to 8 *N*, while the single-electrode potential for the corresponding cerium potentials decreases from approximately 1.44 volts to 1.40 volts in the same range. The latter potential in each case is materially increased by the addition of 5 to 10 ml. of concentrated nitric or perchloric acid—the direct reverse of the effect of similar additions of sulfuric acid to the perchlorate or nitrate titration.

MIXTURE OF FERROUS AND VANADYL PERCHLORATES IN STRONG PERCHLORIC ACID. The use of electrolytically oxidized cerous nitrate or perchlorate in either nitric or perchloric acid solution is inconvenient. Ceric perchlorate and nitrate are not known in crystalline form. The authors have shown that the oxidation of ferrous nitrate in 1 *N* nitric acid gives titration data identical with that of curve B of Figure 2 if a solution of ammonium hexanitrate cerate (8) in 1 *N* nitric acid is used as oxidizing agent. It was therefore proposed to determine whether solutions of the hexanitrate salt in perchloric acid could be used for titrations in perchloric acid media without materially lowering the potentials attained as shown in Figure 3. The differential titration of ferrous

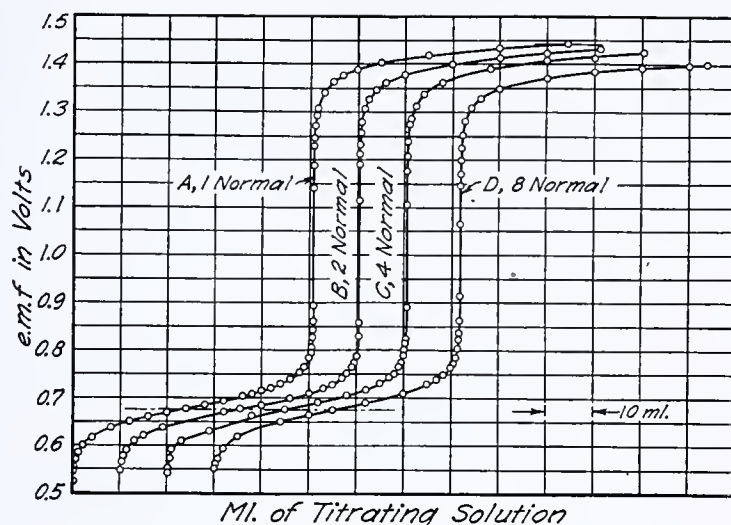


FIGURE 4. TITRATION OF FERROUS SULFATE AT 1 TO 8 *N* SULFURIC ACID STRENGTH

and vanadyl perchlorates in 8 *N* perchloric acid was chosen for illustration, partly because of the practical importance of such a titration, and partly because of the high oxidation potential of the vanadic-vanadyl system which demands a high potential oxidant. A high concentration of perchloric acid was employed to provide the highest potential available. The vanadyl perchlorate was prepared by electrolytic reduction of a solution of vanadic oxide in perchloric acid, using a diaphragm cell, and was free from chloride. Otherwise the titration was conducted as for the ferrous perchlorate titrations. The data are shown graphically in Figure 5. The solutions employed were all approximately 0.05 *N*.

The ferric-ferrous potential attained is 0.825 volt, somewhat lower than in the case of the electrolytically oxidized solutions of cerous perchlorate in perchloric acid. The vanadic-vanadyl electrode potential was found to be 1.23 volts, also an increase in magnitude as compared to the normal electrode potential. The most significant observation, however, is that the potential at equal concentration of tetravalent and trivalent cerium is 1.79 volts, which is 0.23 volt higher than the same potential in 8 *N* nitric acid solutions. The substitution of ammonium hexanitrate cerate for electrolytically oxidized cerous perchlorate can thus be made without great loss in oxidizing intensity. The "break" in e. m. f. for the oxidation of both iron and vanadium is 300 millivolts and leaves nothing to be desired as regards differential selectivity. The amount of vanadium involved (approximately 5.0 mg.) is as much as is ordinarily dealt with in vanadium steel analyses.

### Concepts of Ceric Oxidimetry

The present concepts of ceric oxidimetry involve the assumption of a simple  $\text{Ce}^{++++}/\text{Ce}^{+++}$  ratio of oxidant to reductant. The following are some of the major objections, which point to inconsistencies in this previously accepted theory of ceric oxidimetry:

1. The wide variation in single-electrode potentials determined in hydrochloric, sulfuric, nitric, and perchloric acid solutions, using electrolytically oxidized cerium in the same acids, cannot be satisfactorily explained on the basis of hydrolysis as was postulated by Noyes and Garner (6).

2. Assuming a simple  $\text{Ce}^{++++}/\text{Ce}^{+++}$  ion relationship, the oxidation potentials should not be materially altered by change in the acid concentration. The electrode potentials are observed to decrease with increase in concentration of nitric and sulfuric acids, but increase markedly with increase in perchloric acid concentration.

3. The high single-electrode potentials attained in perchloric or nitric acid solutions can be immediately lowered to potentials approaching those characteristic of sulfuric acid solution by the



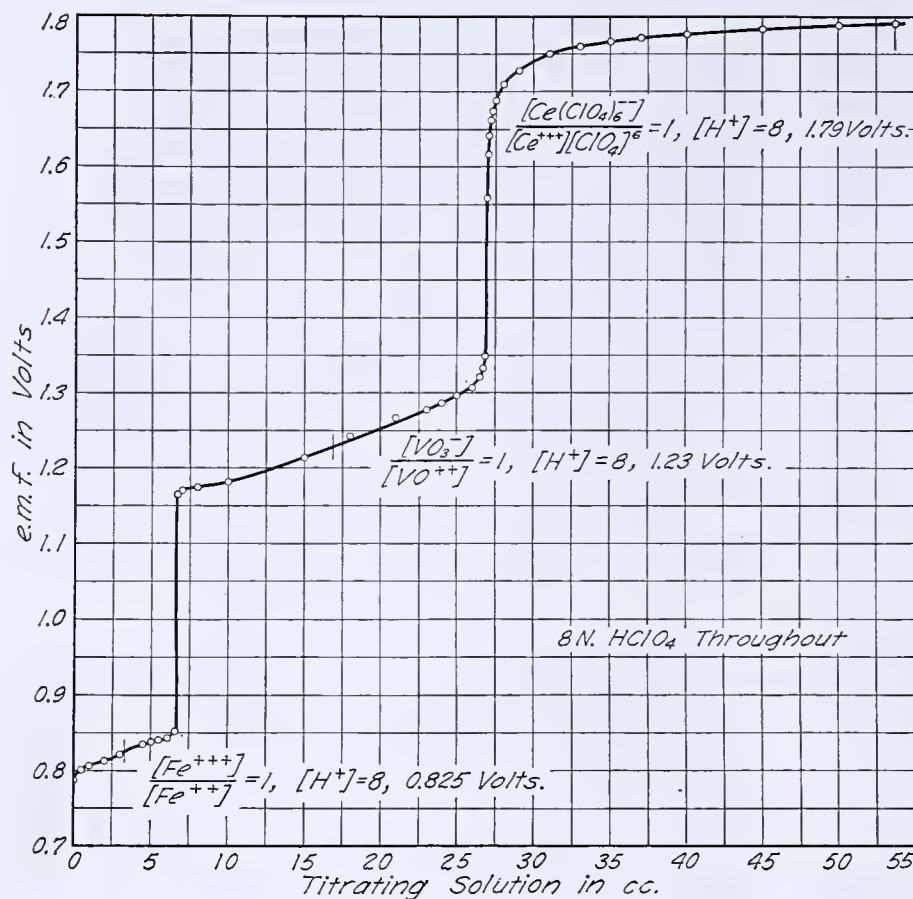


FIGURE 5. TITRATION OF MIXTURE OF FERROUS AND VANADYL PERCHLORATES IN 8 N PERCHLORIC ACID

addition of sulfuric acid in amounts equivalent to the perchloric or nitric acid present.

4. The electrode potential in sulfuric acid solution at standard state can be materially increased, although to a lesser degree than the effect noted under 3, by the addition of nitric or perchloric acid.

**THEORETICAL CONSIDERATIONS.** The experimental work of Meyer and Jacoby (5) on the preparation and properties of ammonium hexanitrate cerate indicates that this product is a complex salt dissociating in solution to give ammonium and nitrate cerate ions. Since the single-electrode potential of this salt at standard state in nitric acid solution is the same as that of cerous nitrate after electrolytic oxidation in 1 N nitric acid, both solutions can be said to owe their oxidizing value to the same ion species. Ceric nitrate in nitric acid solution is then in reality hexanitrate ceric acid,  $\text{H}_2\text{Ce}(\text{NO}_3)_6$ . This product, like its ammonium salt, dissociates in solution to give mainly the nitrate cerate ion,  $\text{Ce}(\text{NO}_3)_6^{--}$ , and hydrogen ions. The ceric-cerous electrode potential relationship instead of a simple  $\text{Ce}^{++++}/\text{Ce}^{+++}$  ratio should be formulated as follows:

$$\frac{[\text{Ce}(\text{NO}_3)_6^{--}]}{[\text{Ce}^{+++}][\text{NO}_3^-]^6} \quad (1)$$

The extent to which tetravalent cerium enters the complex nitrate cerate ion is a function of the nitrate-ion concentration. The potential of this system at 2 N nitric acid concentration is 1.62 volts, which corresponds to the presence of all or most of the tetravalent cerium in the complex nitrate cerate ion. With further increase in nitrate-ion concentration the potential decreases, as would be predicted from an increase in the nitrate-ion concentration in the denominator of the above ratio, until at 8 N nitrate-ion concentration the potential has decreased to 1.56 volts.

Similar reasoning can be applied to electrolytically oxidized cerous perchlorate in perchloric acid solution. The ceric-cerous electrode potential follows the concept of the per-

chlorato cerate ion ratio to the product of the cerous and perchlorate ions:

$$\frac{[\text{Ce}(\text{ClO}_4)_6^{--}]}{[\text{Ce}^{+++}][\text{ClO}_4^-]^6} \quad (2)$$

The degree to which the tetravalent cerium is found as the complex perchlorato cerate ion is again a function of the perchlorate-ion concentration. The highest degree of complex ion formation as shown in Table I has not been attained at 6 or even 8 N perchloric acid strength. At 8 N perchloric acid strength the potential of this system is still increasing, as shown by Figures 1 and 3. Increasing the perchlorate-ion concentration continues to increase the oxidation potential, as the denominator effect is less than that caused by the continued increase in the complexing of the tetravalent cerium.

The ionic relationship expressed in ratio 2 can be converted in large part to that of ratio 1 by the addition of the nitrate ion. In this case the potential of the system decreases.

By analogous reasoning the conditions involving the ceric ion in sulfuric and hydrochloric acid solutions are expressed by the formation of the electrode potential ratios shown in 3 and 4:

$$\frac{[\text{Ce}(\text{SO}_4)_3^{--}]}{[\text{Ce}^{+++}][\text{SO}_4^{--}]^3} \quad (3)$$

$$\frac{[\text{CeCl}_6^{--}]}{[\text{Ce}^{+++}][\text{Cl}^-]^6} \quad (4)$$

and

In ceric solutions at 1 N sulfuric acid concentration the degree of formation of cerate ions is at its maximum, since further addition of sulfuric acid only lowers the potential of the system. (The existence of the complex sulfato cerate ion was postulated by Jones and Soper in 1935, 3. This fact was learned after the completion of this work.) The ceric solutions in hydrochloric acid were studied in the presence of higher hydrochloric acid concentrations, since a precipitate formed before 2 N acid strength was reached.

The experimental procedure in connection with the previously described work does not consider any effect due to the hydrogen ion of the acid media employed. The substitution of nitrate, perchlorate, and sulfate as their alkali salts brings about substantially the same effects. The hydrogen ion of the corresponding acids therefore plays a negligible part.

### Practical Applications in Cerate Oxidimetry

The simultaneous differential titration of ferrous and vanadyl salts has already been shown to be more practical (Figure 5) than any known procedure. While it is possible that, as a result of the high potential attained using perchloric acid solutions of electrolytically oxidized cerous perchlorate or of ammonium hexanitrate cerate, many new and improved volumetric oxidation processes could be devised, two have been thoroughly studied and found advantageous. One is the oxidation of oxalates or the determination of calcium following precipitation as oxalate. The oxalate dissolved in perchloric acid is instantly and quantitatively oxidized to carbon dioxide by use of the hexaperchlorato cerate ion at ordinary temperatures. Ferroin may be used as oxidation indicator in this titration. Proposed methods for the oxidation of arsenite to arsenate, employing cerate



ions as oxidant in perchloric acid solution, are likewise an improvement on former methods. The new oxidizing solutions can be shown to be satisfactorily stable upon storage under ordinary conditions. These facts will be substantiated by subsequent work in this field.

### Summary

The old theory of the mechanism of ceric oxidimetry based upon the assumption of a simple  $Ce^{++++}/Ce^{+++}$  ratio is faulty as a theoretical guide in the interpretation of experimental results.

Tetravalent cerium in nitric and perchloric acid solution as a potential of 1.6 to 1.87 volts, as compared with 1.44 in sulfuric acid solution.

An increase in concentration of perchlorate ion increases the potential; nitrate ion decreases it slightly, and sulfate considerably.

These effects are best explained by assuming the formation of a complex cerate ion.

Potentiometric titrations of ferrous iron in various concentrations of perchloric, nitric, sulfuric, and hydrochloric acid solutions have been carried out and the results compared satisfactorily.

Proposed applications of the new procedures include the

simultaneous differential oxidation of ferrous and vanadyl salts, the improved determination of oxalate including calcium, and the improved titration of arsenite to arsenate.

Cerate oxidimetry in perchloric acid solutions makes available oxidation potentials which are higher than any at present available using a stable standard oxidizing solution—namely, 1.7 to 1.87 volts with reference to the standard hydrogen electrode.

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## Application of the Grignard Reagent to a Study of Mineral Oils

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During a chemical and electrical study of oil oxidation, a Grignard reagent (methyl magnesium iodide) was applied as an analytical tool with some success. By using apparatus similar to the "Grignard machine" currently in use for elucidation of the structure of organic compounds, procedures have been devised which permit the determination of minute amounts of water in oil, the establishment of an oxygen balance during oil oxidation, and the approximate prediction of oxidation stability by a single test on the original oil.

FOR many years, methyl magnesium iodide has found widespread use as an analytical reagent. Zerewitinoff early described its use for determining the number of active hydrogen atoms in an organic molecule by measuring the amount of methane evolved when the substance was treated with an excess of reagent. Later, Kohler and his associates (3, 4) modified this procedure so that not only the amount of methane evolved but also the amount of reagent consumed could be determined. Thus, information can be gained regarding substituents which react with methyl magnesium iodide without evolution of gas. The latter method

was recently modified by Soltys (6) so that it could be used in microanalytical work.

During a chemical and electrical study of the oxidation of insulating oils, the necessity for new analytical methods arose. The Grignard reagent was applied with some success, to a complex mixture such as an oxidized oil, though previous investigators have used it only in the study of pure compounds. While time did not permit an explanation of all the observations, nor perhaps the establishment of optimum conditions for the test, it is hoped that a description of the method and the results will be of some value to the field of petroleum research.

### Apparatus

The apparatus used, shown in Figure 1, is very similar to that described in the literature (3).

The reagent is stored under nitrogen in the reservoir, *H*, and is transferred through *i* to the buret, *J*, as required. The reaction flask, *L*, is constructed from 44-mm. tubing and has a capacity of 50 cc. It is connected to the buret by a standard-taper ground joint at *m*. To ensure intimate mixing of the reagent with the oil, the reaction flask is equipped with a glass stirrer actuated by a solenoid. An intermittent action is obtained by connecting an ordinary dime-store light flasher in the solenoid current supply (110-volt alternating current). The stirrer consists of a 6-mm. tube with an iron nail sealed in the upper end and a cupped flange on the lower end. A pinhole in the tube just below the iron core permits escape of trapped gas. A glass stoppered U-tube filled with Dehydrite is placed between the reaction flask and the gas burets. The first buret, *N*, has a capacity of 20 cc. and is graduated in 0.05-cc. divisions. The second, *O*, is an ordinary 50-cc. gas buret. It is used to accommodate over-

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flow of gas from *N* caused by thermal expansion, and also when large quantities of methane are evolved. The stopcock, *D*, has a special slot to permit the escape of nitrogen to the atmosphere when the system is flushed prior to making a run. The nitrogen is purified by passing it through a hot, reduced copper spiral and the drying train shown in the diagram.

### Procedure

The reagent is prepared from methyl iodide, magnesium, and isoamyl ether as described in the literature (3). Since the solubility of methane in petroleum hydrocarbons is a disturbing factor, standardization of the reagent is best accomplished by adding water to 1 cc. of the reagent in 10 grams of a white oil. In an actual experiment, 1 cc. of reagent produced 8.86 cc. of methane in the presence of oil, and 9.20 cc. when oil was absent. The reagent gives a small but definite blank reading when it is run into the dry flask. This value is constant and can be determined and subtracted from all observed volumes of methane evolved (6, page 112).

The reaction flask and buret *K* are cleaned after use by washing with successive portions of benzene, acetone, dilute hydrochloric acid, distilled water, methanol, and ether, and are dried

by gently heating with a Bunsen flame in a current of air. Ten grams of the oil to be tested are weighed into the dry reaction flask, which is then attached to the buret assembly. The oxygen is swept from the apparatus by passing a rapid stream of purified dry nitrogen through the reaction flask and buret *K* to the atmosphere, for 15 minutes. Stopcock *A* is then closed and the U-tube and connecting capillary tubes are flushed for 5 minutes, the nitrogen being relieved to the atmosphere through the slot of stopcock *D*, the mercury in both burets being held at the zero mark (the base of the stopcock). Stopcocks *B* and *D* are now closed, *C* is opened, and the original gas volume read on buret *N* is recorded. One cubic centimeter of the reagent is now introduced to the reaction flask from *J*. The temperature of the water in the two beakers is recorded, the stirrer is started, and a burner is placed under the beaker surrounding the reaction flask. Stirring is continued for 15 minutes at the temperature of the boiling water in the beaker, the levels in buret *N* having been adjusted to accommodate thermal expansion and evolution of gas. If the expansion is too great to be accommodated in *N*, it is permitted to overflow into *O*, which is returned to the zero mark again on cooling. After heating and stirring are discontinued, the reaction flask is cooled by placing cold water in the beaker. At the end of 30 minutes, the temperature of the water in both beakers is adjusted to the original value, and the increase in volume is noted. After correcting for the reagent blank and the volume of reagent added, this value is recorded as the cubic centimeters of methane produced at the prevailing temperature and pressure. The amount of reagent consumed is

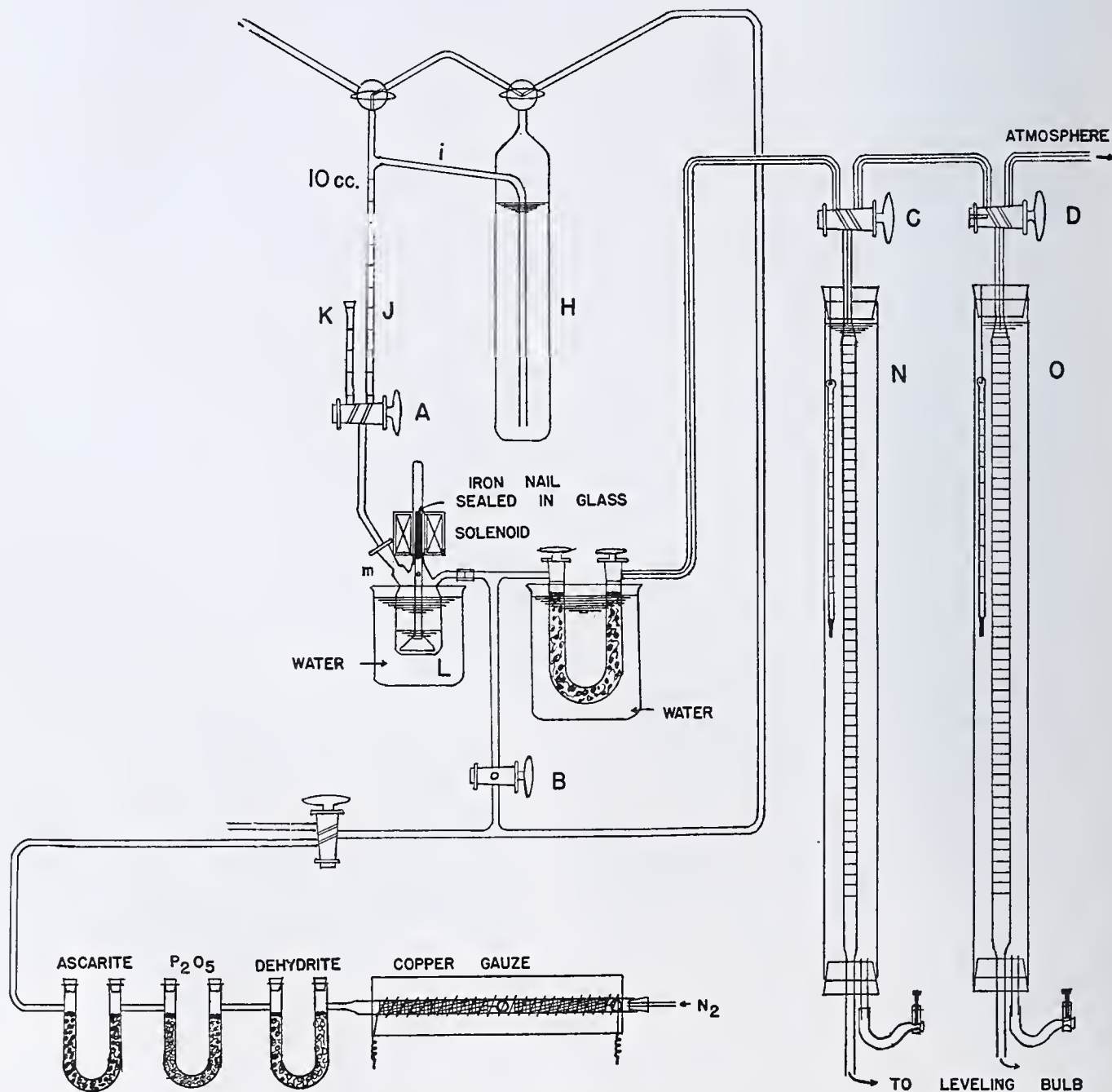


FIGURE 1. GRIGNARD APPARATUS



ext determined by adding 4 cc. of water to the flask through and heating, stirring, and cooling as before. The volume of as produced and the amount of reagent consumed are expressed in millimoles per kilogram of oil at standard conditions.

**ACCURACY.** Since methane is dissolved in petroleum hydrocarbons, the procedure outlined above was adopted to compensate for this factor. Solubility varies slightly for different oils and will thus affect the absolute value of methane evolved. Redissolving of methane is minimized by avoiding agitation of the surface during the cooling period, which should be a uniform time. When a standardized procedure is strictly adhered to, check runs of 0.1 cc. of methane evolved can be obtained. The precise determination of the amount of reagent consumed is more difficult, and accuracy better than 0.2 % of methane cannot be attained; thorough agitation is important since the solutions are heterogeneous.

### Determination of Water

From an electrical standpoint, the presence of minute amounts (0.01 per cent or less) of water is of importance, and development of a sensitive test was imperative. The magnesium nitride method of Boisselet and Rachkani (1), the upper acetylide test, the use of water-soluble oil-insoluble reagents, the calcium hydride method (2), and the distillation method of Rodman (5) were considered. The last method was the most acceptable but possessed the disadvantage of requiring large samples. Since methyl magnesium iodide reacts with water to produce methane, it was tried and found to give satisfactory results. Table I summarizes the results obtained by adding weighed amounts of water to an anhydrous neutral commercial insulating oil; the initial blank reading obtained on the oil is discussed below.

TABLE I. DETERMINATION OF WATER

Sample	Water Added %	Gas Evolved at N. P. T.		Water Found %
		Cc.	% Water	
Original oil	None	1.09	0.0087	
Sample 1	0.0044	1.58	0.0127	0.004
Sample 2	0.010	2.38	0.0191	0.010
Sample 3	0.017	2.94	0.024	0.015

To use this method, it is first necessary to determine the blank value for the particular oil under observation by weighing a portion of it; this is done very effectively by spraying the oil into a vacuum of approximately 1 mm. at 100° C. Using the value thus obtained, the water content of subsequent samples can readily be determined. When the percentage of water only is of interest, it is unnecessary to use standardized reagents or to determine the amount of reagent consumed. If the water content of a badly oxidized oil is considered, the determination will be high but can readily be corrected if the acid value is known. Since there is no suitable means of checking the results of this determination on actual samples, it is impossible to evaluate the accuracy of the test under these conditions. In several instances the relation between electrical losses and the amount of methane produced was good and, when other tests were considered, justified the conclusion that very small amounts of water were detected by this method.

### Forming an Oxygen Balance

To evaluate properly the oxidation of oils, it is helpful to know the proportions in which the various oxidation products are formed—i. e., what part of the total amount of oxygen consumed in the process appears in each type of oxidation product. The Grignard reagent is useful for this purpose when used in connection with other tests. The amount of methane produced is a measure of the amount of acids, al-

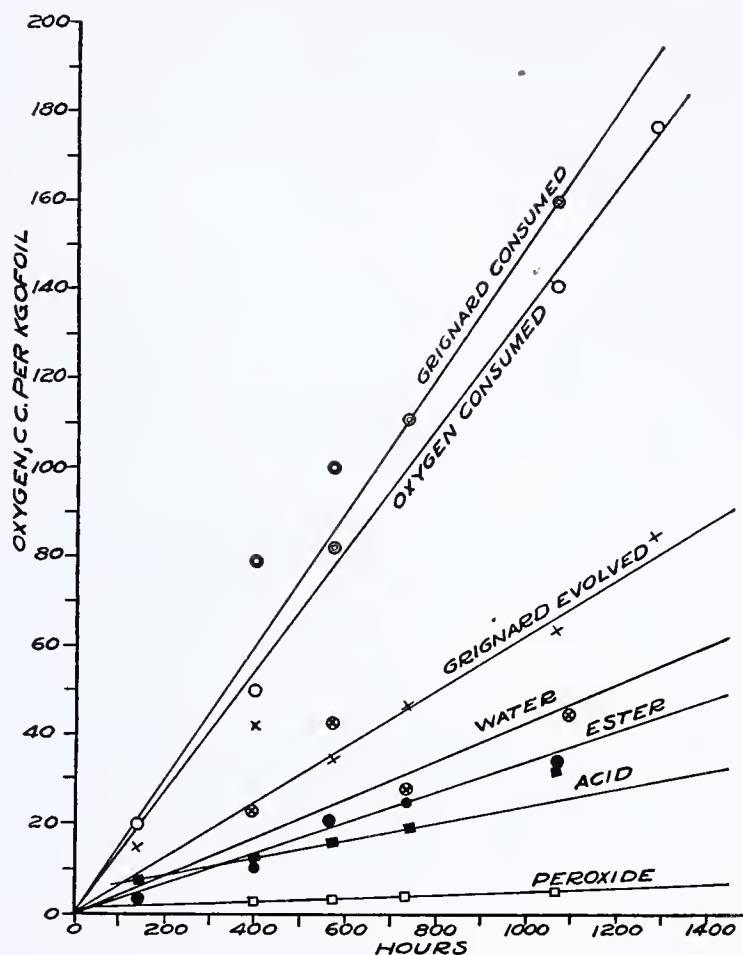


FIGURE 2. OXYGEN BALANCE, OIL A

cohols, and water present. The amount of reagent consumed is an indication not only of these substances, but of all other oxidation products, such as peroxides, esters, aldehydes, and ketones, and is therefore an indication of the total content of oxidized molecules. Since the molar ratio of reagent consumed to oxidized molecules present is not always unity, the experimentally determined value will not represent the true value, but it is a useful approximation.

Figure 2 shows the oxygen balance for the oxidation of a commercial insulating oil in a closed system at 120° C. The water determinations were made by the method of Rodman (5). Acids and esters (hydrolyzable substances) were determined by titration using the glass electrode in *n*-butanol. Peroxides were determined by their oxidation of ferrous sulfate, followed by reduction of the ferric ion with standard titanous chloride. The amount of methane evolved is very nearly equal to the sum of the water plus the acid content, from which it is concluded that the alcohol content is small. A sufficiently sensitive test for alcohols in the presence of other oxidation products could not be found to afford a verification of this conclusion. Figure 2 also shows that the amount of reagent consumed when expressed as equivalent volume of oxygen is approximately equal to the experimentally determined value for the oxygen absorbed. The initial values for water content, methane evolved, and reagent consumed were all greater than zero and were subtracted from subsequent values to bring the curves through the zero point. The relationships shown are typical in general for a large number of oils examined.

### Oxidation Stability

As mentioned earlier, a dry unoxidized oil produces considerably more methane when treated with methyl magnesium iodide than can possibly be accounted for on the basis



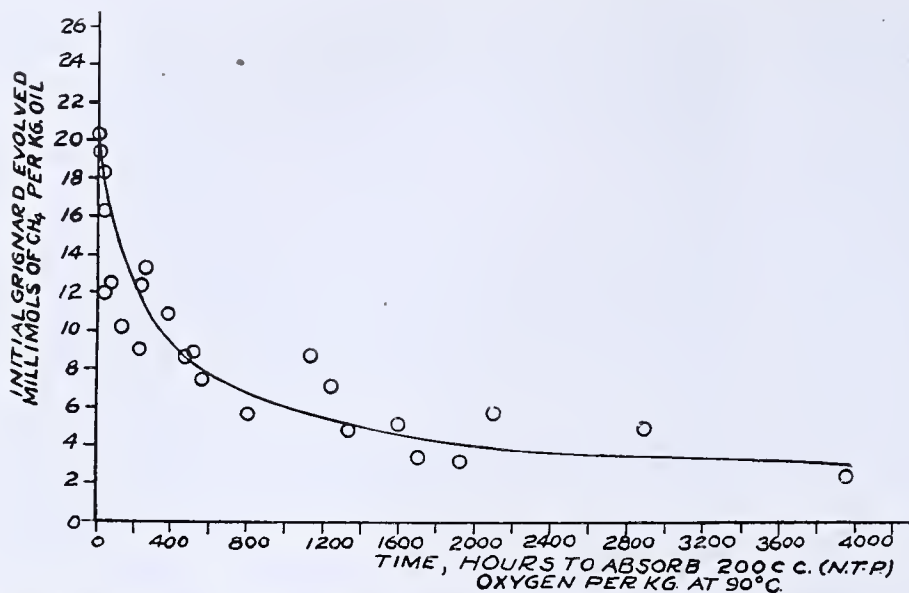


FIGURE 3. METHANE EVOLVED PRIOR TO OXIDATION vs. OXIDATION TIME

of extraneous contamination. This initial production of methane varies for different oils, decreasing roughly as the degree of refining is increased. After oxidation rates of several oils had been studied, it became apparent that a relationship exists between the amount of methane evolved in the Grignard test on the original oil and the subsequent rate of oxidation.

The results are shown graphically for 24 oils in Figure 3. These oils are representative of petroleum oils in general, ranging in viscosity from 84 to 1504 Saybolt seconds at 100° F. (37.78° C.). Viscosity indexes range from 4 to 122. The oils were obtained from representative crudes of the four major oil fields in the United States and were refined by almost every method in commercial use—distillation, acid treatment, aluminum chloride, DuoSol, phenol, furfural, sulfur dioxide, and Chlorex. In view of the wide variation in the initial properties of the oil, such as peroxide content and unsaturation values, and the fact that many of the ox-

idation rates were extrapolated to the same temperature (90° C.) though determined at widely different temperatures, the correlation is significant.

Evidence was acquired which demonstrates that this evolution of gas when an oil is treated with methyl magnesium iodide is a property of the normal constituents of the oil. This is shown by the fact that this initial evolution of gas was not appreciably altered by any of a series of successive operations, such as degassing, distillation, clay treatment, and heating with sodium, which might be expected to remove water and oxidation products. It can only be suggested here that the correlation arises from reaction with sulfur compounds, reaction with active hydrocarbons of the indene type, or deep-seated decomposition reactions catalyzed by the magnesium complex.

### Acknowledgment

This study is part of a joint research on the oxidation stability and electrical characteristics of insulating oils being conducted by the Electrical Engineering Department of the Massachusetts Institute of Technology and the Utilities Coordinated Research, Inc., under the auspices of the Association of Edison Illuminating Companies. The author wishes to express his appreciation to them and to J. C. Balsbaugh for his interest and coöperation.

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RECEIVED January 24, 1938.

## Preservation of Oleum Samples

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THE need is often felt for some manner of holding samples of oleum without any possibility of deterioration until some future time when they can be analyzed without interruption of routine laboratory schedules.

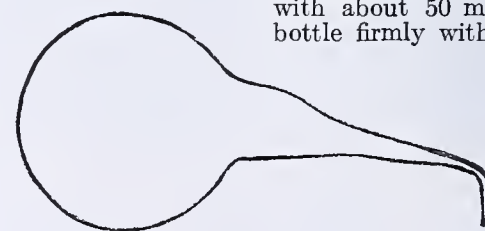
The following method was developed in this laboratory, so that samples of oleum might be taken from tank cars with no possibility of loss of gases or of absorption of water and preserved in their original condition until they could be handled without interfering with the routine laboratory work.

Small glass bulbs are blown in the gas flame from 10-mm. tubing with the general shape of a retort, necked out about 5 cm. (2 inches) to a fine capillary point, and having a capacity of 4 or 5 ml. With a little practice these bulbs can be turned out successfully.

Tare the bulb, then heat in the drying oven or hold near the gas flame until the inside air is thoroughly heated. Have a laboratory assistant pour some of the oleum into a small beaker at this point. Now grasp the bulb a short distance back of the tip and insert in the liquid. As the heated air in the bulb cools, the resulting vacuum will draw in the sample of oleum. (From 1 to 2 grams is generally satisfactory for use with normal acid and may be soon estimated for succeeding analyses.)

Carefully seal the bulb tip in the gas flame, taking care to lose no glass. When cool carefully wipe off the tip or rinse with distilled water, then put aside for drying until the analysis can be conveniently fitted in with the laboratory routine. When ready for analysis, drop the reweighed bulb into a wide-mouth 16-ounce (approximately 500-ml.) bottle in which a known excess of sodium

hydroxide has been pipetted and diluted with about 50 ml. of water. Close the bottle firmly with a rubber stopper and break the sealed bulb with a quick sharp shake against the inverted bottom. Continue shaking until all the gas is dissolved. Then lift the stopper slightly,



wash down the sides with distilled water, and titrate the excess sodium hydroxide with normal acid.

If a blank has been previously run against the sodium hydroxide, the amount of hydrochloric acid equivalent to the sample is easily computed. At this plant 20 per cent oleum is in use, and the results are calculated to per cent sulfuric acid.

RECEIVED March 4, 1938.



# The Exudation Test for "Bleeding" in Bituminous Roofing

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"Bleeding," or "strike-through," by which is meant the exudation of unsightly black spots occasionally noted on the surface of ready roofing, is due to a peculiar type of incompatibility, as yet unexplained, between the asphalt used as saturant and that used as coating. During the last 7 years the author has developed an "exudation test" for determining this lack of compatibility between the saturant and the coating, before their use in roofing manufacture.

IN THE manufacture of ready roofing a felted sheet is saturated with a hot, relatively soft bituminous saturant. The excess of saturant is removed and a substantial layer of relatively hard blown asphalt coating compound is applied in molten condition to both surfaces of the hot saturated sheet. Intimate contact between the coating and saturant is thus obtained. Granules may be applied to the upper surface of the hot coated sheet to protect the coating from actinic light and to decorate the product. The finished sheet may then be cut into shingle shapes or shipped in rolls. In either event the layers of the finished goods are tightly packed at a slightly elevated temperature.

In case asphalts have been used that prove incompatible in the sense just described, "bleeding," or "strike-through," begins to develop in the warm package, and continues steadily, not only after the product has cooled but also after application and exposure to solar heat. It is first noted as small, dull-black spots, that appear to have exuded through the minute pores, or pinholes, that frequently occur in the coating layer or at the edges of the roofing sheet. In time, new spots appear, while the old ones grow steadily wider and may eventually assume a glossy black color and a soft and oily consistency. Eventually some of the spots may run together to form large black blotches all over the roofing sheet and will even strike through the wrapping paper around the package. The progressive development of bleeding is shown in Figure 1 (a, b, and c).

Although in extreme cases the surface of the product and the package may present a very unsightly appearance, the exudation is not particularly apt to cause sticking in the package, as the spots appear to be less sticky than oily in character. Furthermore, after exposure for a few months during hot summer weather, the slow accumulation of dust on the surface and the effects of weathering gradually obscure these black spots both on smooth and on granule-covered roofing, until they are hardly discernible. This fading of the oily spots on exposure is illustrated in Figure 1. *d* shows the under side of a granule-surfaced shingle which displayed marked bleeding after a period of exposure; *e* shows the granule-covered surface of the same shingle. On *e* the bleeding spots are visible on the upper portion which was protected by the superimposed shingle, but they have practically disappeared on the lower portion which was exposed directly to the weather.

There is evidence that when asphalts that are incompatible in the sense above indicated are placed in contact with one another at room temperatures, there will develop at the interface between the two a very thin layer of bitumen, of a softer consistency than either, but that this film will remain permanently at the interface until it is encouraged to migrate outward by capillarity, as when pinholes are present in the coating layer, or when a layer of dusting has been applied at or adjacent to the interface or to the pores in the coating. This outward migration results in the scattered black spots typical of bleeding in roofing.

These bleeding phenomena should not be confused with the normal exudation of very thin oily matter that occurs on the surface of all blown asphalts on aging. For example, no bleeding whatever will occur, even when a coating is of the type that develops an extremely oily surface on aging, if that coating is used with a compatible saturant. On the other hand, if the saturant is not compatible, marked bleeding can occur even when the coating is of the type that does not readily develop an oily surface on aging.

## Exudation Test

The exudation test, that has been developed by the author to detect this strike-through tendency as between any saturant and any coating, consists simply in applying a drop of the

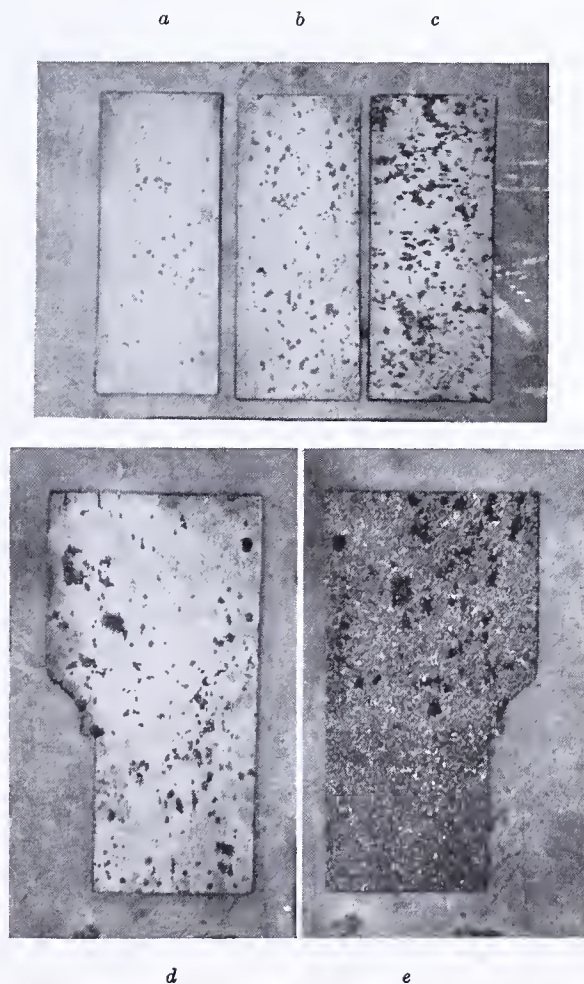


FIGURE 1. ROOFINGS ILLUSTRATING PROGRESSIVE DEVELOPMENT OF BLEEDING IN STORAGE, AND EFFECTS OF EXPOSURE



saturant to the talc-dusted surface of the coating, maintaining the latter at a temperature of  $43.33^{\circ}\text{C}$ . ( $110^{\circ}\text{F}$ .) for 72 hours, and measuring the width of the black ring of discolored talc that forms around the periphery of the spot. In an effort to standardize the conditions of the test, the following technic has been developed:

The coating is warmed to a fluid condition. It may then be poured into the lid of a 3-ounce (88.7-ml.) penetration tin or other convenient receptacle in a layer 0.3 to 0.6 cm. (0.125 to 0.25 inch) thick. To remove air bubbles the surface of the coating may be momentarily heated. The surface area and total weight of the specimen are determined and the surface is then given a preliminary dusting with fine roofer's talc, evenly distributed over the surface, neither the surface nor the talc being handled by the fingers during this operation. The excess of nonadherent powder is removed by inverting the specimen and allowing the container to drop 2.5 cm. (1 inch) onto the table top. A second application of fine talc is then made by gently shaking or tapping a 300-mesh sieve held 7.5 cm. (3 inches) above the surface of the specimen, so that a fine mist rather than agglomerated particles of the powder may accumulate on the specimen. This operation is continued with occasional weighings until a uniform film of talc weighing 0.025 gram per square inch (6.45 sq. cm.) has been obtained. Uniformity in the thickness of the talc film is of great importance in obtaining reproducible results, for the thicker the layer of talc (up to a certain limit), the wider will be the ring formed.

A drop of the saturant about 0.16 cm. (0.0625 inch) in diameter is placed upon the talc-dusted surface of the coating. This may be done most conveniently by plunging the end of a heated spatula or paring knife into the cold saturant and, after the excess has drained off, allowing a drop of suitable size to fall on the dusted surface from a height of about 1.25 cm. (0.5 inch). Several drops of the same or different saturants may be applied to a single specimen of dusted coating.

The specimen is then placed in an oven maintained at a temperature of  $43.33^{\circ} \pm 2.8^{\circ}\text{C}$ ., ( $110^{\circ} \pm 5^{\circ}\text{F}$ .) for a period of 72 hours. With some asphalts that are entirely free from strike-through tendencies towards each other, no reaction whatever will occur in this test, except for the very slow flattening of the spherical drop and the gradual yellowing of the dusting. With other asphalts that do have strike-through tendencies, the drop will flatten more rapidly; and relatively early in the test a thin ring of a darker color than the surrounding area will form on the dusted surface right around the periphery of the drop, and will grow wider blacker, and glossier, till it reaches a maximum width and gloss characteristic of that combination of asphalts, and of that type and quantity of dusting, after which it spreads and darkens no further.

The average width of the dark-brown or black ring of discolored talc that has formed at the end of 72 hours around the periphery of the spot is determined to the closest 0.1 mm. by means of a scale of suitable dimensions and a good magnifying glass. This dark ring is usually sharply defined, and the vague penumbra that sometimes develops beyond the area of marked discoloration should be disregarded. A roughly quantitative estimate of the degree of bleeding to be anticipated in roofing in which any two asphalts are to be used, may be based on the width of ring of discolored talc that they develop in the exudation test. If no ring whatever is formed in that test not the least traces of bleeding will occur in the roofing made with the two asphalts.

Although the technic described above has been found to be most reliable and convenient for routine work, many variations may be made in the method of test. For example, fine and coarse dustings of limestone, silica, mica, lamp-black, slate, wood flour, asbestos, and other fibrous and non-fibrous products have been used with some degree of success, though some will form a wider and some a narrower ring than an equally thick layer of talc. On the other hand, the total absence of dusting on the surface of the coating in the

test will prevent the formation of the characteristic ring, even when a film of the exudate is known to be present between the two asphalts involved.

The effect of time and temperature in curing the specimen has also been investigated. The completion of the reaction will require weeks at room temperature. At  $43.33^{\circ}\text{C}$ . ( $110^{\circ}\text{F}$ .) the reaction will be substantially complete in about 3 days. Twenty-four hours at  $60.0^{\circ}\text{C}$ . ( $140^{\circ}\text{F}$ .) and 5 hours at  $79.44^{\circ}\text{C}$ . ( $175^{\circ}\text{F}$ .) will give, very roughly, the same results as 3 days at  $110^{\circ}\text{F}$ .; but the interfluxing of the coating, saturant and exudate that occurs at temperatures higher than  $110^{\circ}\text{F}$  is objectionable and mars the distinctness of the reaction. Hence,  $110^{\circ}\text{F}$ . for 3 days was finally decided on.

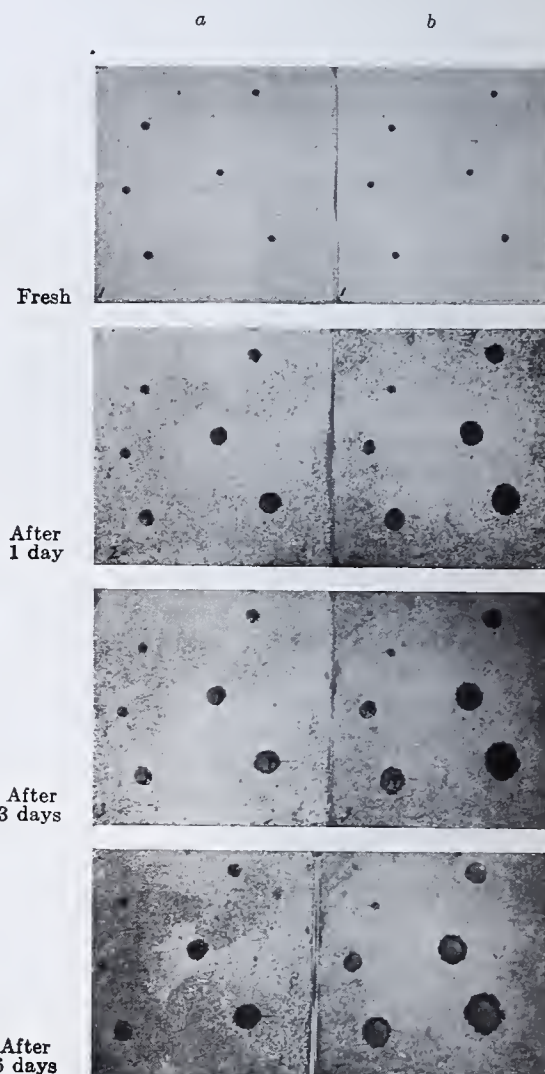


FIGURE 2. PROGRESSIVE STAGES OF EXUDATION TEST

The progressive development of the exudation reaction at  $110^{\circ}\text{F}$ . is demonstrated in Figure 2 by means of two square panels of coating shown in the successive stages of the test. The coating used on panel *a* differed as to source from that used on panel *b*, but both coatings were of approximately 20 penetration and  $98.89^{\circ}\text{C}$ . ( $210^{\circ}\text{F}$ .) melting point (ring and ball). The two panels were coated and prepared in the standard manner described above. Three varieties of hard saturant (H1, H2, and H3) were applied one below the other in that sequence on the left-hand side of each panel, and three soft saturants (S1, S2, and S3) were applied similarly on the right-hand side. The source and method of processing were different for each of the saturants, except that H3 and S2 were both produced by vacuum distillation from the same crude.



The consistencies of the six saturants were as follows:

Saturant	Penetration	Saturant	Penetration
H1	30	S1	150-175
H2	65	S2	150-175
H3	40	S3	150-175

The pictures at the top of Figure 2 show the two panels before they were placed in the oven. The second set, immediately below, shows their condition after exposure for one day at 110° F.; the third and fourth sets, after 3 and 6 days' exposure, respectively. It will be observed that no colored ring was formed on either coating around saturant H1. However, saturants H3, S2, and S3 developed rings on both coatings, while saturants H2 and S1 developed rings on coating B but not on coating A. The rings widen with time to a definite maximum, and when the test is conducted at 110° F. they are of substantially maximum width at the end of 3 days. The average width of ring for each of the twelve combinations illustrated in Figure 2 is given in Table I.

TABLE I. WIDTH OF RING

Saturant	On Coating A			On Coating B		
	After 1 day	After 3 days	After 6 days	After 1 day	After 3 days	After 6 days
	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
Hard	H1	0.0	0.0	0.0	0.0	0.0
	H2	0.0	0.0	0.25	0.35	0.65
	H3	0.15	0.25	0.3	1.2	2.0
Soft	S1	0.0	0.0	0.75	1.0	1.0
	S2	0.25	0.7	1.8	2.9	3.4
	S3	0.9	1.5	1.7	2.6	4.7

Several years of practical experience with the exudation test have led to the conclusion that while it is safest practice to use only saturants and coatings that show no ring whatever in that test, no visible bleeding will occur in roofings made with a saturant and coating that in the standard exudation test at 110° F. develop a ring not wider than 0.5 mm.

RECEIVED January 12, 1938.

# Internal Electrolysis without Diaphragms

## Determination of Small Amounts of Nickel, Cobalt, and Copper in Ores Poor in These Metals

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THE authors (7) have shown the advantages of internal electrolysis over external electrolysis in the determination of small amounts of metals, and have pointed out that a very simple apparatus without diaphragm may be substituted for the complicated apparatus, proposed by a number of authors (2, 4, 5, 11, 12), without impairing the accuracy of the analysis (6, 9, 10).

In addition (1) having selected a suitable anode, we obtain a definite potential difference not exceeded at any moment during the course of the electrolysis but very slowly and gradually diminishing by 0.1 to 0.2 volt. Therefore by internal electrolysis it is possible to make separations which by external electrolysis require a constant control of the anode potential and a suitable apparatus. (2) The chief side process occurring at the anode is the dissolution of the anode with the formation of the corresponding ions of this metal in the solution. This eliminates many difficulties of electrolysis due to the oxidation at the anode of a number of substances to their higher valency states.

We are therefore justified in hoping that small amounts of nickel and cobalt may be separated from large quantities of iron and from chromium by this method. This was the chief purpose of the present work.

### Apparatus

The apparatus for internal hydrolysis used by the authors is shown in Figure 1 (and in Figure 1 of an earlier article, 7). The anode is a Fischer's platinum gauze; the anode is a metallic plate of iron, zinc, or aluminum, depending on the metal to be precipitated and on the conditions of precipitation. To secure a good contact, the electrodes are firmly held together by a copper or aluminum clamp, which replaces the copper wire formerly used and somewhat simplifies manipulations. The places of contact must always be well cleaned with emery paper before proceeding to work.

### Determination of Nickel and Cobalt

The normal potentials ( $E_0$ ) of nickel, cobalt, and iron are:  $E_{Ni/Ni^{++}}$ , 0.25 volt;  $E_{Co/Co^{++}}$ , 0.255 volt;  $E_{Fe/Fe^{++}}$ ,

0.44 volt) would indicate that nickel and cobalt would be deposited on the platinum cathode, if the anode were an iron plate. The potential difference, 0.19 volt, is sufficient for such a deposition. However, because of the very small overvoltage of hydrogen on nickel and cobalt, these metals cannot be deposited by electrolysis in an acid medium, while in ammoniacal solutions they form complex ions, as a result of which their potentials are shifted and become more negative than in an acid medium.

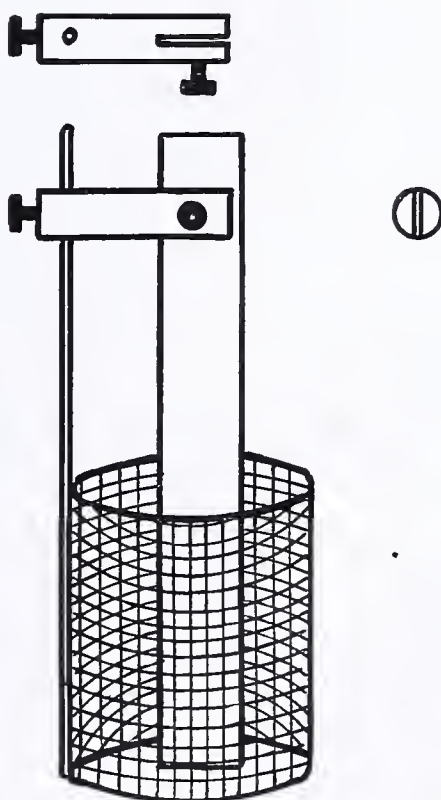


FIGURE 1



The authors failed to separate nickel and cobalt by using an iron anode in an acid (acetic or oxalic acid) or ammoniacal solution. Neither were these metals fully deposited from an ammoniacal tartrate medium.

The attempt to deposit nickel or cobalt on the cathode, using cadmium and chromium plates in a feebly acid and an ammoniacal medium, was also unsuccessful, evidently because of an insufficient potential difference. Using a zinc anode, the two metals were fully deposited.

To a solution containing a definite amount of nickel and cobalt sulfates, 10 grams of ammonium sulfate and 15 ml. of concentrated ammonia were added, the solution was diluted to 150 to 200 ml. and heated to 70° C., and bound electrodes (Pt-Zn) were placed in the solution. The electromotive force of this cell determined by the compensation method at the beginning was found to be equal to 0.60 to 0.58 volt. After 30 to 35 minutes (Figure 2) it gradually falls to 0.50 volt, and then remains constant. Nickel and cobalt are deposited quantitatively during this time. A test for the completeness of deposition, made by adding sodium sulfide to the electrolyte after the electrolysis, showed no traces of nickel and cobalt.

TABLE I. DETERMINATION OF NICKEL AND COBALT FROM SOLUTIONS OF THEIR SULFATES

No.	Introduced		Found		
	Nickel Gram	Cobalt Gram	Nickel + cobalt Gram	Nickel Gram	Cobalt Gram
1	0.0027	....	....	0.0027	....
2	0.0027	....	....	0.0028	....
3	0.0027	....	....	0.0026	....
4	0.0027	....	....	0.0028	....
5	0.0054	....	....	0.0054	....
6	0.0060	....	....	0.0060	....
7	0.0081	....	....	0.0074	....
8	0.0107	....	....	0.0083	....
9	....	0.0025	....	....	0.0026
10	0.0025	0.0003	0.0030	0.0027	0.0003
11	0.0025	0.0003	0.0019	0.0026	0.0003
12	0.0025	0.00055	0.0031	0.0026	0.0005
13	0.0025	0.00055	0.0031	0.0026	0.0005
14	0.0025	0.0011	0.0036	0.0025	0.0011
15	0.0025	0.0011	0.0037	0.0026	0.0011
16	0.0025	0.0017	0.0042	0.0025	0.0017
17	0.0025	0.0017	0.0043	0.0026	0.0017
18	0.0027	0.0025	0.0052	0.0027	0.0025

Nos. 7 and 8. Cementation on the anode.  
 Nos. 9 to 18. Cobalt determined in the deposit colorimetrically; nickel, by difference.

Table I indicates that in the absence of other metals nickel and cobalt are completely deposited on the cathode when present in amounts not exceeding 6 to 7 mg. A number of experiments (including Nos. 7 and 8) have helped to establish that larger quantities of nickel and cobalt begin cementation on the zinc anode, leading to results that are too low.

However, an active metal like zinc as the anode furnishes conditions suitable for the deposition of all the metals nobler than zinc, if present in the solution. In the ores under investigation, only copper, chromium, and iron were present.

Less than 3 per cent of iron does not interfere with the electrolytic deposition of nickel and cobalt, since under the conditions of the electrolysis it is present in the form of a small precipitate of hydroxide, not decomposed by the current. With an iron content of over 3 per cent, the precipitate of hydroxide is so bulky that the adsorption of cobalt and

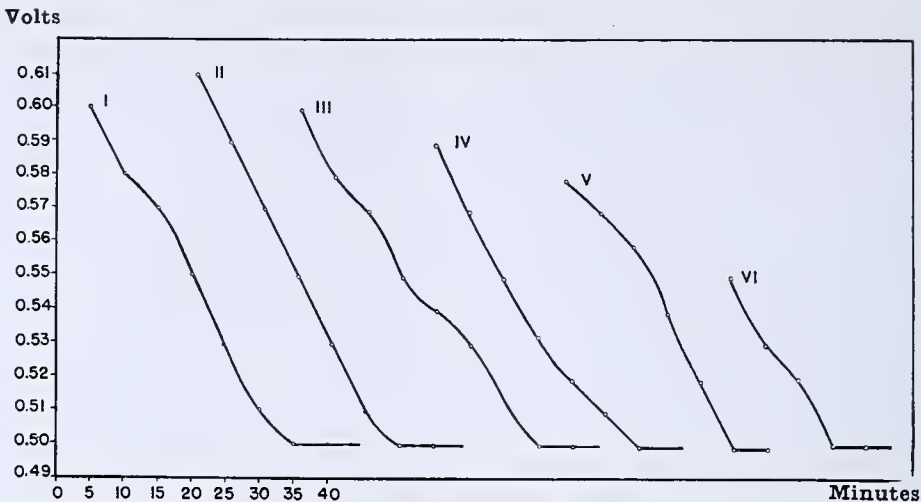


FIGURE 2

nickel by the precipitate affects the results of determination.

DETERMINATION OF THE PRESENCE OF IRON. To eliminate the influence of iron the authors have tried combining with stable complex compounds by the action of pyrophosphate, tartaric acid, oxalic acid, potassium cyanide, and sodium fluoride.

The first three, as shown by numerous experiments, do not give complexes stable under the conditions and do not prevent the deposition of iron on the cathode.

With potassium cyanide, iron, nickel, and cobalt form such stable complexes that they are not deposited from the solution. The only complex-former yielding good results has been found to be sodium fluoride, combining with ferric iron to form a stable complex  $\text{FeF}_6^{--}$  and exercising no influence upon nickel and cobalt salts.

To a solution containing nickel and ferric salts, acidified with sulfuric or acetic acid, 2 grams of sodium sulfate or acetate were added (to increase the electric conductivity of the solution) the solution was diluted with water to 100 ml., and 50 to 60 ml. of a sodium fluoride solution saturated in the cold were added. Then 2 to 3 drops of phenolphthalein and ammonia were added until a pink coloration appeared (a large excess of ammonia should be avoided as it diminishes the stability of the complex ferric fluoride). The solution was diluted to 200 ml., the electrodes (Pt-Zn) were placed in it, and it was subjected to internal electrolysis for 35 to 40 minutes.

Figure 3 shows that the potential difference at the beginning is equal to 0.57 to 0.60 volt, then it gradually diminishes, and after 35 to 40 minutes stops at 0.42 volt. At this point no nickel is detected in the solution. The nickel deposited on the cathode has a dark color, and the results, as shown by Table II, are too high, owing to the coprecipitation of fluorides

TABLE II. DEPOSITION OF NICKEL IN THE PRESENCE OF IRON AND FLUORIDES

No.	Introduced		Nickel Found	
	Nickel Gram	Iron Gram	After first deposition Gram	After second deposition Gram
1	0.0027	0.15	0.0039	0.0026
2	0.0027	0.15	0.0042	0.0028
3	0.0027	0.15	0.0047	0.0026

To secure good results, the authors dissolved the deposit of nickel and redeposited it. The connected electrodes were removed from the electrolyte bath, washed with distilled water (by dipping for some seconds in a glass of water), then disconnected the deposit of nickel was dissolved by immersing the cathode in a glass containing 20 ml. of sulfuric acid (1 to 4), and the clear cathode was washed with hot water over the glass. After adding an excess of 10 to 15 ml. of ammonia, and diluting the solution to 150 to 200 ml., it was again subjected to electrolysis for 35 to 40 minutes at 70° C. When deposition was complete, the electrodes were removed, washed with water, and disconnected, and the cathode was washed with alcohol and dried at 80° to 90° C.

As shown by the last column in Table II, the results of the second deposition are satisfactory.

In Table III are compiled the results of nickel and cobalt determinations in the presence of iron under the conditions specified above.



TABLE III. DETERMINATION OF NICKEL AND COBALT IN THE PRESENCE OF LARGE AMOUNTS OF IRON

Cobalt in the deposit was determined colorimetrically; nickel, by difference)

No.	Introduced			Found		
	Nickel Gram	Cobalt Gram	Iron Gram	Nickel + cobalt Gram	Nickel Gram	Cobalt Gram
1	0.0025	0.00015	0.15	0.0026	0.0025	0.00012
2	0.0025	0.0003	0.15	0.0028	0.0025	0.0003
3	0.0025	0.0005	0.15	0.0030	0.0025	0.0005
4	0.0025	0.0005	0.15	0.0030	0.0025	0.0005
5	0.0025	0.0011	0.15	0.0036	0.0025	0.0011
6	0.0021	....	0.15	0.0020	0.0020	....
7	0.0016	....	0.15	0.0017	0.0017	....
8	0.0011	....	0.15	0.0011	0.0011	....
9	0.0006	....	0.15	0.0006	0.0006	....

TABLE IV. DEPOSITION OF NICKEL IN THE PRESENCE OF CHROMIUM

No.	Introduced		Nickel Found Gram	Observations
	Nickel Gram	Chromium Gram		
1	0.0027	0.0034	0.0025	Nickel deposited in 1 hour
2	0.0027	0.0057	0.0020	Nickel deposited in 1 hour
3	0.0027	0.0079	0.0000	No nickel at all deposited

DETERMINATION IN THE PRESENCE OF CHROMIUM (AND LARGE QUANTITIES OF IRON). Since in many poor nickel ores the chromium content is only about 0.3 to 0.5 per cent, the authors had to study nickel and cobalt deposition by internal electrolysis in the presence of chromium. The experiments were made with salts of tri- and hexavalent chromium, and helped to establish the fact that chromium is not deposited on the cathode, but that when present in small amounts it retards the deposition of nickel and cobalt and large amounts prevents deposition.

The authors succeeded in eliminating the influence of chromium, oxidizing it, and precipitating it by salts of chromium (acetate or chloride) under the following conditions:

To a solution containing salts of nickel, ferric iron, and hexavalent chromium, 5 ml. of acetic acid, 2 grams of sodium acetate or greater electric conductivity of the solution), and 2 to 3 ml. of a 10 per cent solution of barium chloride were added (five times the quantity theoretically required for precipitation). The solution was allowed to stand for 5 to 10 minutes for a better separation of barium chromate; and without filtering off the precipitate to 60 ml. of a saturated sodium fluoride solution were added; the solution was neutralized with ammonia by means of phenolphthalein, diluted to 150 to 200 ml. with water, heated to 70° C., and subjected to internal electrolysis as described above with a deposition of nickel and cobalt from the ammoniacal sulfate solution.

TABLE V. DETERMINATION OF NICKEL AND COBALT IN THE PRESENCE OF CHROMIUM AND LARGE QUANTITIES OF IRON

Cobalt in the deposit was determined colorimetrically; nickel by difference)

No.	Introduced				Found		
	Nickel Gram	Cobalt Gram	Iron Gram	Chromium Gram	Nickel + cobalt Gram	Nickel Gram	Cobalt Gram
1	0.0005	....	0.10	0.009	0.0005	0.0005	....
2	0.0010	....	0.10	0.009	0.0010	0.0010	....
3	0.0015	....	0.10	0.009	0.0014	0.0014	....
4	0.0027	....	0.10	0.006	0.0026	0.0026	....
5	0.0027	....	0.10	0.009	0.0026	0.0026	....
6	0.0027	....	0.10	0.015	0.0026	0.0026	....
7	0.0027	....	0.10	0.015	0.0027	0.0027	....
8	0.0027	....	0.10	0.030	0.0028	0.0028	....
9	0.0025	....	0.10	0.009	0.0025	0.0025	....
10	0.0025	0.0005	0.10	0.009	0.0030	0.0025	0.0005
11	0.0025	0.0005	0.10	0.009	0.0030	0.0026	0.0004
12	0.0025	0.0005	0.10	0.009	0.0030	0.0026	0.0004
13	0.0025	0.0005	0.10	0.009	0.0030	0.0026	0.0004
14	0.0025	0.0005	0.10	0.009	0.0031	0.0026	0.0005
15	0.0025	0.0005	0.10	0.009	0.0030	0.0026	0.0004

The results given in Table V indicate that the method is satisfactory for ores of the usual chromium content.

### Determination of Copper

The third metal interfering with the deposition of nickel and cobalt by internal electrolysis is copper.

To determine copper in ores by internal electrolysis (7), copper was deposited in an acetic acid solution in the presence of hydrazine (to eliminate the disturbing influence of ferric ions), using a lead plate as the anode. The method could not be applied without modification, since lead, passing to solution from the anode plate during the determination of copper, would interfere with a further determination of cobalt and nickel, being deposited on the cathode with these metals.

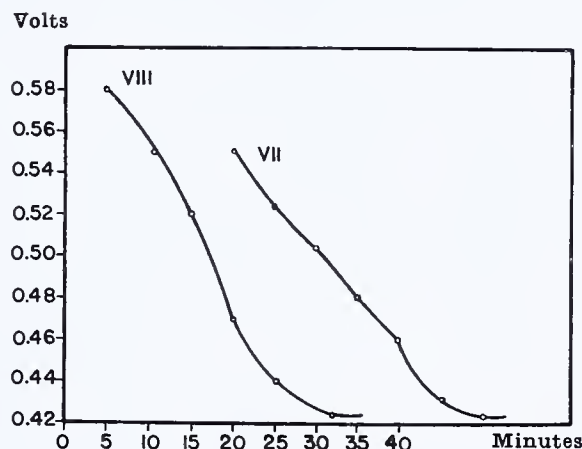


FIGURE 3

To overcome this difficulty the authors investigated two possibilities: (1) deposition of copper from an acid solution using a zinc plate as the anode and employing sodium fluoride to eliminate the influence of ferric iron, and (2) deposition of copper from an acid solution with the aid of an iron anode. The first modification seemed especially attractive, as no new foreign metals were introduced into the solution, and before determining nickel and cobalt only a neutralization of the solution with ammonia was necessary.

A number of experiments were carried out with solutions of salts of copper, nickel, and iron in an acetic acid and a feebly sulfuric acid medium (Table VI).

TABLE VI. DETERMINATION OF COPPER IN THE PRESENCE OF NICKEL, COBALT, AND IRON WITH A ZINC ANODE, IN AN ACID MEDIUM

(Volume of solution, 200 ml. Nos. 1 to 4, 10 ml. of free acetic acid. Nos. 5 and 6, 10 drops of 1 to 1 free sulfuric acid)

No.	Introduced				Copper Found	
	Copper Gram	Nickel Gram	Cobalt Gram	Iron Gram	After first deposition Gram	After second deposition Gram
1	0.0145	0.0026	0.0005	0.10	0.0170	0.0139
2	0.0145	0.0026	0.0005	0.10	0.0165	0.0140
3	0.0145	0.0026	0.0005	0.10	0.0163	0.0144
4	0.0145	0.0026	0.0005	0.10	0.0163	0.0139
5	0.0145	0.0026	0.0005	0.10	Not determined	0.0139
6	0.0145	0.0026	0.0005	0.10	Not determined	0.0140

In all cases the copper first deposited was of a dark color, and its weight was too high. After dissolving the deposit from the cathode in dilute nitric acid and redeposition with the lead anode, the results in the majority of cases were too low. In the electrolyte after the second deposition considerable amounts of nickel were detected. In addition, the zinc anode during the first deposition was coated with a marked layer of copper, which seems to account for the too low ultimate results obtained for copper.

Thus, the first modification proved unsuccessful for the following reasons: (1) because of the large difference between the potentials  $E_{Zn/Zn^{++}}$  and  $E_{Cu/Cu^{++}}$  the copper is to a considerable extent cemented on the anode; (2) in the



presence of copper, nickel is partly deposited with it, in spite of the relatively high acidity of the solution, as the over-voltage of hydrogen on the surface of copper plus nickel is obviously greater than that on the surface of pure nickel.

To study the conditions of deposition of copper by the iron cathode (the second modification), a number of experiments were made in an acetic and a sulfuric acid solution (Table VII).

TABLE VII. DEPOSITION OF COPPER BY THE IRON ANODE  
(Volume of solution, 200 ml.)

No.	Introduced			Copper Found		Conditions of Deposition
	Copper	Nickel	Iron	After first deposition	After second deposition	
	Gram	Gram	Gram	Gram	Gram	
In Acetic Acid Solution						
1	0.0145	0.0025	..	0.0132	....	80% acetic acid, 4 ml.
2	0.0145	0.0025	..	0.0132	....	
3	0.0145	0.0025	..	0.0134	....	
4	0.0145	0.0025	..	0.0130	....	
5	0.0145	0.0025	..	0.0144	....	80% acetic acid, 6 to 10 ml.
6	0.0145	0.0025	..	0.1044	....	
7	0.0145	0.0025	0.10	0.0150	0.0132	Iron combined by sodium fluoride; 80% acetic acid, 10 ml.
8	0.0145	0.0025	0.10	0.0158	0.0135	
9	0.0145	0.0025	0.10	0.0156	0.0132	
10	0.0145	0.0025	0.10	0.0158	0.0140	
11	0.0145	0.0025	0.10	0.0156	0.0132	80% acetic acid, 10 ml. Fe <sup>+++</sup> reduced by hydrazine
12	0.0145	0.0025	0.10	0.146	....	
13	0.0145	0.0025	0.10	0.144	....	
In Sulfuric Acid Solution						
14	0.0145	0.0025	..	0.0143		H <sub>2</sub> SO <sub>4</sub> (1:1), 2 drops
15	0.0145	0.0025	..	0.0144		H <sub>2</sub> SO <sub>4</sub> (1:1), 3 drops
16	0.0145	0.0025	0.10	0.0137		Iron combined with NaF; H <sub>2</sub> SO <sub>4</sub> (1:1), 3 drops
17	0.0145	0.0025	0.10	0.0136		
18	0.0145	0.0025	0.10	0.0143		Iron combined with NaF; H <sub>2</sub> SO <sub>4</sub> (1:1), 2 to 4 ml.
19	0.0145	0.0025	0.10	0.0144		
20	0.0145	0.0025	0.10	0.0144		Iron reduced by hydrazine

In a feebly acetic acid solution (experiments 1 to 4) copper is not entirely deposited. Good results are obtained only with an acidity of 6 to 10 ml. of 80 per cent acetic acid to 200 ml. of solution (experiments 5 and 6). To eliminate the influence of ferric ions, combination with fluoride or reduction by hydrazine was used. In the first case the copper deposited was black, and the results obtained were too high (experiments 7 to 11). In these cases repeated depositions led to results that were too low, as in the first modification. When Fe<sup>+++</sup> was reduced by hydrazine, the results were satisfactory (experiments 12 and 13); the color of the deposit was pink. In a feebly sulfuric solution, in the absence of iron, copper is deposited quantitatively (experiments 14 and 15), an acidity of 2 to 3 drops of sulfuric acid (1 to 1) in 200 ml. being sufficient. Satisfactory results are obtained in this medium also in the presence of iron, if the latter has been reduced by hydrazine (experiment 20). Iron may also be combined with sodium fluoride, but in this case the acidity should be raised to 2 to 4 ml. of sulfuric acid (1 to 1) in 200 ml. (experiments 18 and 19).

TABLE VIII. DETERMINATION OF COPPER, NICKEL, AND COBALT IN THE PRESENCE OF LARGE AMOUNTS OF IRON

(Nos. 1 to 3 iron reduced by hydrazine; nos. 4 to 7 iron combined with fluoride. Cobalt determined colorimetrically by the method of Lurie and Troitzkaja (8); nickel, by difference)

No.	Introduced			Iron Gram	Found			Conditions of Depositing Copper
	Copper Gram	Nickel Gram	Cobalt Gram		Copper Gram	Nickel Gram	Cobalt Gram	
1	0.0145	0.0025	0.0005	0.10	0.0144	0.0026	0.0005	5% acetic acid
2	0.0145	0.0025	0.0005	0.10	0.0143	0.0024	0.0004	
3	0.0145	0.0025	0.005	0.10	0.0144	0.0026	0.0005	
4	0.0129	0.0026	0.0005	0.10	0.0129	0.0026	0.0004	H <sub>2</sub> SO <sub>4</sub> (1:1), 4 ml. to 200 ml. of solution
5	0.0129	0.0026	0.0005	0.10	0.0129	0.0025	0.0005	
6	0.0129	0.0026	0.0005	0.10	0.0129	0.0026	0.0004	
7	0.0129	0.0026	0.0005	0.10	0.0129	0.0026	0.0005	

Thus, the authors have obtained two methods for the deposition of copper by internal electrolysis with an iron anode in the presence of nickel (cobalt) and iron: in a 4 to 5 per cent acetic acid solution in the presence of hydrazine, and in a 1 per cent sulfuric acid solution in the presence of fluorides or hydrazine. After the deposition of copper and before the determination of nickel and cobalt in the electrolyte, the

excess of hydrazine and ferrous iron ions should be oxidized. If hydrazine is not used, and iron has been combined with fluoride, an additional oxidation is still necessary, since the solution contains ferrous iron, due to the dissolution of the iron anode. The oxidation was brought about by means of bromine, the excess of which was eliminated by boiling. Then the solution was cooled, sodium fluoride (a saturated solution) or solid ammonium fluoride was added, and nickel and cobalt were determined under conditions described above.

The results are given in Table VIII, which shows that copper, nickel, and cobalt are deposited quantitatively. The method is very accurate, but the oxidation of hydrazine, if used, proved slow.

As in internal electrolysis, previous to the deposition of copper, a reduction of ferric iron occurs in the solution at the expense of the current itself [at the cathode, 2 Fe<sup>+++</sup> + 2 e → 2 Fe<sup>++</sup>; at the anode, Fe (from the anode) − 2 e − Fe<sup>++</sup>], the authors decided to try depositing copper in the presence of iron without any other reducing agents by increasing the time of electrolysis and by a greater dissolution of the anode. In the presence of less than 0.1 gram of iron such a method has given good results. With a higher iron content considerable cementation of copper on the anode occurs because of the excessive time of electrolysis.

### Aluminum Anode

Although aluminum has a very negative normal oxidation potential, E<sub>0</sub> = −1.34, an aluminum anode in internal electrolysis behaves like an iron anode: without depositing nickel and cobalt, it deposits copper very well. Aluminum does not increase the content of ferrous ions in the solution to be later oxidized, and its solubility in a 1 per cent acid is less than that of iron. During electrolysis, aluminum dissolves to a very small extent, which diminishes the consumption of fluorides for combining iron and aluminum before the nickel and cobalt determination. The cementation of copper on aluminum is exceedingly small: on a smooth polished aluminum surface it has not been observed at all; on a rough surface, it is negligible.

As a result of these investigations, the authors have developed the following procedure for analysis of ores containing small amounts of copper, nickel, and cobalt.

### Procedure

In the absence of chromium or when it is present in quantities less than 3 mg., the procedure is as follows:

**DETERMINATION OF COPPER.** The ore sample, 0.5 or 1 gram depending on the nickel content (the amount of nickel in the sample should not exceed 6 mg.), is treated with 10 ml. of hydrochloric acid (d = 1.19), then with 5 ml. of nitric acid (d = 1.4); 5 to 6 ml. of sulfuric acid (1 to 1) are added, and the whole is evaporated in a dish to fumes of sulfuric acid.

To the slightly cooled residue 20 to 30 ml. of water are added, and the mixture is boiled to dissolve salts. Then the solution is neutralized with ammonia to the first appearance of a permanent precipitate of ferric hydroxide, which is dissolved with a few drops of dilute (1 to 1) sulfuric acid, an excess of 4 ml. being added. The contents of the dish are transferred to a 400-ml. beaker, diluted with hot water to 200 ml., and heated to 60° to 70° C. (If the iron content exceeds 0.1 gram, it is reduced by adding 1 gram of hydrazine.)

After placing the connected electrodes (Figure 1) in the solution with a previously weighed platinum cathode and an iron or aluminum plate serving as the anode, electrolysis is carried on for 30 minutes at 60° to 70° C. Then 10 to 20 ml. of water are added and the electrolysis is continued for 10 minutes more. When deposition is complete (the part of the electrode covered again with the liquid should remain pure), the electrodes are removed from the beaker, washed over the beaker with a jet of water from a washing bottle, and disconnected; the cathode



washed with alcohol, dried for 5 minutes at 80° to 90° C., and weighed.

The difference in the weight of the cathode shows the copper content of the sample.

**DETERMINATION OF NICKEL AND COBALT.** After the deposition of copper, bromine is added to the electrolyte until the solution is brown; the solution is then boiled to remove the excess of bromine and to reduce the volume of the solution to 100 ml.

After cooling the solution slightly, 50 to 60 ml. of a sodium fluoride solution saturated in the cold (about 4 per cent) are added, to 3 drops of phenolphthalein are then added, and the solution is neutralized with ammonia until a pink coloration develops, a brown precipitate where the first drops of ammonia fall is evidence of insufficient sodium fluoride; in such a case a little more sodium fluoride solution is added). The solution is heated to 70° C., the electrodes are placed in it (the cathode being a platinum gauze, and the anode a zinc plate), and the solution is subjected to electrolysis for 30 to 35 minutes (the completeness of deposition is tested by adding water).

If the bromine has been poorly removed, the deposition of nickel and cobalt may be somewhat retarded, and 0.2 to 0.3 gram sodium sulfite should be added to the solution.

After nickel and cobalt have been completely deposited, the electrodes are removed, washed by dipping in a beaker of distilled water, and disconnected, and the cathode is dipped in a beaker containing 20 ml. of sulfuric acid (1 to 4). When the deposit is dissolved, the cathode is taken out and washed with hot water over the beaker. To the solution 10 to 15 ml. excess of concentrated ammonia are added and the solution is diluted to 150 to 200 ml. and heated to 70° C. The electrodes (Pt-Zn) are connected again, the cathode having been previously weighed, and placed in the solution, which is subjected to electrolysis for 35 to 40 minutes. When deposition is complete, the electrodes are removed and disconnected, and the cathode is washed with alcohol, dried for 5 minutes at 90° to 100° C., and weighed. The increase in the weight of the cathode shows the sum of nickel plus cobalt.

**COLORIMETRIC DETERMINATION OF COBALT (8).** The deposit on the cathode is dissolved in 20 ml. of nitric acid (1 to 1). The cathode is washed with hot water over the beaker, and the solution is evaporated to dryness. The evaporation is repeated once more, after adding 10 ml. of hydrochloric acid; the residue is leached with 1 to 2 ml. of hydrochloric acid (1 to 1) and diluted with a few milliliters of hot water. To the solution, which should have a volume of about 10 ml., a few crystals of ammonium thiocyanate and a little sodium sulfite are added. It is heated (at 60° to 80° C.) until green (the color of a nickel salt). Upon cooling, 1 gram of sodium pyrophosphate, 1 to 2 drops of phenolphthalein, and dilute (12 per cent) ammonia are added, the latter being introduced in drops, until the color of the solution has changed to pink. Then 5 grams of ammonium thiocyanate are added (the pink coloration disappears), the solution is diluted to 100 ml., and thoroughly shaken; 15 ml. of pure acetone and 1 to 2 drops of dilute ammonia are added, and the whole is vigorously stirred for 1 to 2 minutes. The solution is allowed to stand for 3 to 5 minutes and poured into an Eggerz test tube. To another test tube the same reagents are introduced in the same quantity, and a standard cobalt chloride solution is added from a buret until the color, after stirring, matches that of the test solution. From the number of milliliters of the standard solution of cobalt salt added, the cobalt content of the sample is calculated.

The nickel content of the sample is calculated by deducting the cobalt content found from the sum of nickel plus cobalt, obtained by internal electrolysis.

In the presence of more than 3 mg. of chromium, copper is deposited in the same way as in the absence of chromium.

TABLE IX. ANALYSIS OF ORES

No.	—Sample 52 Found in—			—Sample 36 Found in—		
	Copper	Nickel	Cobalt	Copper	Nickel	Cobalt
	%	%	%	%	%	%
1	0.58	0.59	0.012	0.32	0.30	0.0065
2	0.58	0.61	0.013	0.32	0.31	0.0065
3	0.58	0.58	0.013	0.32	0.31	0.0065
4	0.58	0.60	0.012	..	..	..
5	0.58	0.58	0.013	..	..	..
6	0.58	0.58	0.012	..	..	..

When ferrous iron is oxidized with bromine, as described above, 1 gram of ammonium persulfate is added, and the solution is boiled 10 minutes or until the oxidation of Cr<sup>+++</sup> to Cr<sub>2</sub>O<sub>7</sub><sup>---</sup> and the decomposition of the excess of ammonium persulfate are complete. (The oxidation of Fe<sup>++</sup> and Cr<sup>+++</sup> with ammonium persulfate should not be made at the same time, to avoid intro-

ducing excessive SO<sub>4</sub> ions to the solution.) After this, 30 per cent barium chloride solution is added until barium sulfate is completely precipitated. The precipitate is filtered off through a filtering crucible with suction and washed with a small amount of hot water.

The filtrate is evaporated down to a volume of 100 ml., cooled, neutralized with ammonia, and acidified with acetic acid (an excess of 3 to 5 ml. of 80 per cent acetic acid). To make sure precipitation of barium chromate is complete, 1 to 2 ml. more of barium chloride are added; the mixture is allowed to stand for 10 minutes, and without filtering off the precipitate a sodium fluoride solution is added. The further procedure is similar to that in the absence of chromium.

The method has been verified on two samples of ore (Table IX).

The results obtained precisely check with those obtained by the usual methods. Aside from the elements enumerated, the following were found in ores: SiO<sub>2</sub>, 41 to 42%; Fe<sub>2</sub>O<sub>3</sub>, 18 to 19%; Al<sub>2</sub>O<sub>3</sub>, 22%; CaO, 8 to 9%; Pb, 0%; Zn, 0%; As, 0%; Sb, 0%; Cr, 0.4%; Sn, 0%; S, 2%; W, V, Mn, absent; Mg, 2.5%.

## Conclusions

Nickel and cobalt cannot be deposited by internal electrolysis with an iron, cadmium, or chromium anode, because of the shifting of potentials of these metals in an ammoniacal medium.

The internal electrolysis method for the deposition of nickel and cobalt with a zinc anode gives accurate results.

In order to deposit nickel and cobalt in the presence of ferric iron, a sodium fluoride iron complex must be formed, which is not decomposed in a feebly ammoniacal medium.

Up to 3 mg. chromium does not interfere with the determination of nickel and cobalt by internal hydrolysis; with more than 3 mg. of chromium the deposition of nickel and cobalt is retarded or ceases altogether. The interference of chromium is eliminated by precipitating it as barium chromate.

When copper is present, it should be separated first. The separation of copper from nickel by internal electrolysis with the aid of a zinc anode in a feebly acid medium is not feasible, because of the co-deposition of nickel with copper on the cathode.

Copper may be deposited and determined in a 1 per cent sulfuric acid solution with the aid of an iron or aluminum anode.

Less than 0.1 gram of iron does not interfere with the deposition of copper; a larger quantity of iron must be combined with sodium fluoride or reduced by hydrazine.

The determination of nickel, cobalt, and copper by internal electrolysis without diaphragms in ores poor in these metals yields very accurate results, agreeing with those obtained by more complicated methods.

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# Determination of Sulfur in Oil

## Tetrahydroxyquinone As an Indicator in Direct Titration

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SULFUR in oil is usually determined by the barium sulfate precipitation method as prescribed by the American Society for Testing Materials (2). Analytical chemists have long sought a substitute to allow savings in time, and the investigators feel that the method presented here fulfills this requirement.

Previous publications (5, 6, 7) specified a dispersion of tetrahydroxyquinone in potassium chloride. Further research on the method of preparation of the indicator indicates that with certain other dispersing agents the end point of the titration was materially improved, the end-point range was sharpened, and the color change was intensified. The use of tetrahydroxyquinone dispersed in an organic medium (THQ) has been found to overcome the difficulties mentioned by Ampt (1), Manov (4), and Gibson (3).

The determination of sulfur in oil is important in the examination of petroleum and there is a wide field of application for a rapid and accurate method. In the method proposed the oxidation of sulfur in a bomb according to standard methods is followed by complete oxidation by bromine (2), concentration of sample to a definite volume, and direct titration of an aliquot with standard barium chloride solution, using tetrahydroxyquinone as an internal indicator. The color change is sharp from yellow to red. The method requires only about 0.75 hour as compared with 3 or 4 hours for a gravimetric analysis, and gives results obtainable within the limits as specified by the A. S. T. M. (2) and by most laboratories.

The indicator used throughout this study is a dispersion of the disodium salt of tetrahydroxyquinone in a solid organic medium, and is manufactured in the Betz laboratories with the modifications mentioned. This product is anhydrous and stability tests for sensitivity and color reaction have indicated no changes in its properties in 8 months.

TABLE I. COMPARISON OF METHODS

Sample	Sulfur			Difference Allowed, A. S. T. M.	
	Gravimetric analysis %	THQ %	Average difference %	Same operator %	Different operator %
100-ml. Sample					
1	0.67	0.67			
	0.68	0.68	0.00	0.05	0.07
2	1.09	1.08			
	1.08	1.08	0.01	0.06	0.11
3	0.55	0.52			
		0.51	0.03	0.04	0.06
4	0.18	0.20			
		0.20	0.02	0.03	0.04
5	0.23	0.24			
		0.23	0.01	0.03	0.04
6	0.31	0.29			
		0.28	0.02	0.03	0.04
7	1.97	1.90			
		1.90	0.07	0.10	0.18
8	0.17	0.17			
		0.16			
		0.15	0.01	0.02	0.03
200-ml. Sample					
9	0.71	0.67			
		0.71	0.02	0.05	0.08
10	0.15	0.17			
		0.17	0.02	0.03	0.03
11	1.94	1.86			
		1.80	0.11	0.10	0.17
12	1.47	1.40			
		1.37	0.08	0.08	0.13
13	0.43	0.39			
		0.43	0.02	0.04	0.05
14	0.28	0.25			
		0.28	0.01	0.03	0.04
15	1.97	1.89			
		1.89	0.08	0.10	0.18

MATERIALS AND REAGENTS. Standard barium chloride solution, 1 ml. = 0.0004 gram of sulfur, standardized gravimetrically by precipitation as barium sulfate

Potassium hydroxide 0.02 *N* (approximately)

Hydrochloric acid 0.02 *N* (approximately)

Phenolphthalein indicator, 1 per cent solution

Tetrahydroxyquinone indicator

Ethyl alcohol, or ethyl denatured by formula 30 or 3-A, or isopropyl alcohol

Measuring dipper, capacity 0.15 gram of indicator

PROCEDURE. Take a sample of oil weighing from 0.6 to 0.9 gram, record the weight, and burn in an oxygen bomb. Treat the sample thus obtained with bromine water in the conventional manner (2). Evaporate sufficient water to bring the total volume of the sample below 100 ml., cool, and make up in a volumetric flask to 100 ml. Transfer 25 ml. of sample by pipet to a 125 ml. Erlenmeyer flask, add a few drops of phenolphthalein indicator, and neutralize just to the alkaline side of the phenolphthalein end point with approximately 0.02 *N* potassium hydroxide. Discharge the red coloration with approximately 0.02 *N* hydrochloric acid. Add 25 ml. of alcohol, and 1 dipper of indicator (0.15 gram). Titrate the sample with standard barium chloride solution until the solution changes sharply from yellow to red that is permanent with strong shaking. Shake the flask throughout the titration to establish equilibrium conditions.

CALCULATION OF RESULTS. From the total volume of the barium chloride required, 0.1 ml. should be subtracted for a blank. The amount of sulfur present in the original sample may then be calculated from the following formula:

$$\frac{\text{Ml. of BaCl}_2 \times \text{strength of BaCl}_2 \text{ (in grams of sulfur per ml.)}}{\text{weight of oil sample in grams}} \times 100 \times 4 = \text{per cent of sulfur in oil}$$

In the examination of this method, duplicate samples were burned in a bomb, and the sulfur content of the oil was determined gravimetrically on one set in accordance with the usual A. S. T. M. procedure, while the other set was analyzed for sulfur by the method presented here. Results obtained are presented in Table I.

Samples 9 to 15, inclusive, were evaporated to below 200 ml. volume and made up to 200 ml., and 25 ml. were taken for titration. In this case, a factor of 8 was required. While results obtained with the use of a 200-ml. volume are acceptable, the increased time required for evaporation to the 100-ml. volume is justified by finer results. The variance is practically each case with the 100-ml. sample was less than half the limits as set by A. S. T. M. for different operators and in all cases less than the variance allowed for the same operator, and at the same time well within limits allowed by the oil companies. After evaporation and adjustment to the proper volume, the time required for a determination is less than 5 minutes. On the basis of these data, this method can be used by oil laboratories for the routine control of sulfur in oil, expecting checks at all times within acceptable limits. While the data presented cover only petroleum oils, the method should be applicable to marine and vegetable oils and possibly to certain other organics.

### Summary

Sulfur in oil can be determined following the usual oxidation of an oil sample in a bomb, by direct titration using tetrahydroxyquinone as an internal indicator. Results obtained are well within the limits as prescribed by the American Society for Testing Materials (2).



an Society for Testing Materials and maintained by most oil companies; and the method is suggested for routine determination of sulfur in oil to effect a saving in time without sacrifice of accuracy.

### Acknowledgment

The authors gratefully acknowledge the generous aid of V. H. & L. D. Betz and their permission to publish this study. The collaboration of George A. Shaner and his assistance in preparing the oil samples is sincerely appreciated.

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# Determination of Inorganic Salts in Crude Oils

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A NUMBER of different methods of extracting the inorganic salts from crude oil for their subsequent analysis are in use, all of which seem to be either long and tedious, unreliable, or both. The most widely used procedure for extracting the salt from crude oil is the so-called U. O. P. method (3). In this method, the salt is removed by agitating the oil with benzene, water, and acetone, the acetone presumably being used to cause coalescence of the emulsified particles of brine in the oil and to prevent emulsification of the extract when water added.

This method is capable of giving sufficiently accurate results for most practical purposes if two or three extractions of the oil sample are made. With some crudes, one extraction may be sufficient, but the time required for complete separation of the oil and water phases and the necessity for drawing and analyzing all the aqueous phase are objectionable features. An aliquot portion of the separated aqueous phase cannot immediately be taken for analysis, since the total volume of the aqueous phase is unknown until it has been completely separated and measured, which usually takes some time. The acetone added is distributed between the oil and water and the distribution ratio varies with the specific kind of oil under examination. Also, some of the acetone is added after agitation of the mixture and before drawing off the aqueous phase, and may or may not become distributed between the oil and water in equilibrium amounts.

In another frequently used method, the oil is shaken with benzene and water for several minutes and the mixture is then centrifuged to separate the aqueous layer, which is drawn off and analyzed. Since a definite amount of water may be added, a measured portion of the separated aqueous extract may be analyzed and the total salt content calculated. However, it has been found by repeated tests in this laboratory that this method is completely unreliable. The salt content determined by analysis of this extract is almost invariably low, with one crude giving as little as 18 per cent of the actual salt content. To remove the salt completely from most oils, agitation alone with water is not sufficient.

The presence of salts in crude oil almost invariably means that the oil contains emulsified brine. The 1 per cent or less of emulsified brine contained in refinery stocks generally consists of extremely fine droplets (often less than  $10^{-4}$  cm. in diameter) which are highly stabilized by an adsorbed film of emulsifying agent normally occurring in the oil. These droplets do not coalesce readily with one another or with added water unless they are destabilized in some manner.

A new method of extraction has been developed in this laboratory which is fairly rapid and gives nearly quantitative removal of the salt in one extraction. With this method, de-

stabilization of the brine emulsion and prevention of emulsification of the extraction water are brought about by the use of a small amount of a destabilizing chemical compound. From tests with a large number of different destabilizing chemicals and many different oils, it has been found that the most generally useful compound is a mixture of the ammonium salts of isomeric sulfonic acids of high molecular weight, the exact structures of which are unknown. These sulfonic acids are characterized by the fact that their calcium and magnesium salts have appreciable water solubility. The mixture of ammonium salts of these acids is available under the trade name of Destabilizer A.<sup>1</sup>

### Procedure

Into a 750- or 1000-ml. separatory funnel put 100 ml. of the crude oil, 100 ml. of xylene, and 4 ml. of a 5 per cent xylene solution (or the equivalent if other than a 5 per cent solution is used) of Destabilizer A. Shake for 30 seconds and add 100 ml. of boiling, chloride-free, distilled water. Stopper the funnel and shake, releasing the pressure occasionally at first, for a total time of 5 minutes. Then allow to stand. Break up any loose emulsion which may collect at the oil-water interface by gentle agitation with a long stirring rod. Draw off as much of the aqueous layer as is required for analysis, filter to remove any oil film, and analyze measured portions of the extract by conventional methods (1).

When the salt content of an oil is low, it is advisable to extract larger samples of oil, using proportionately larger amounts of xylene, water, and destabilizer.

Since the distilled water is added at a temperature near 100°C. and since the temperature of the separated aqueous extract will have fallen nearly to room temperature by the time the portions are taken for analysis, the volume of the water added will have decreased by about 4 per cent by this time. Therefore, the total volume of the aqueous layer at the time of measurement of the portions taken for analysis will be 96 ml. plus the small volume of brine originally dispersed in the oil. Account of this fact should be taken in calculating the total amount of any constituent in the sample based on the analysis of a measured portion of the aqueous extract.

### Discussion of Procedure

Use of the large separatory funnel is recommended in order that a large free space may be present to permit violent agitation of the liquids during shaking.

The amount of the destabilizer used is very important. The amount called for in the procedure has been found suffi-

<sup>1</sup> Analysts may obtain reasonable amounts of this material and of Destabilizer B gratis, from the Tretolite Company.



cient for all oil samples analyzed in this laboratory. Less destabilizer is sufficient with some oils, but since the use of this material does not interfere with subsequent analyses for halogens and cations, it is safer to use the amount given. Use of too little of this destabilizer results in poor separation of the oil and water and incomplete extraction of the brine.

TABLE I. EFFECT OF AGITATION ON AMOUNT OF SALT EXTRACTED

(Total halogen as mg. of NaCl per liter of crude)

3 min.	Agitation Time		
	5 min.	10 min.	15 min.
From Shuler Crude			
906	975	1000	1000
931	1006	994	1013
855	969	988	..
925	956	..	..
From Oklahoma Crude			
147	149	151	..
144	149	143	..
145	153	149	..

Since the calcium and magnesium salts of most sulfonic acids are partially soluble in oil, it was feared at first that much of the calcium and magnesium would be lost by solution in the form of sulfonates in the oil phase. The destabilizer called for in the procedure is equivalent to roughly 30 mg. of calcium chloride or 25 mg. of magnesium chloride, which often is more than is present in 100 ml. of crude. To determine whether or not this occurred, the following test was made:

A solution was prepared containing about 1 gram of calcium chloride per liter and 100 ml. of this solution were analyzed for calcium by the usual gravimetric method (1). Another 100-ml. portion was shaken for 10 minutes with a mixture of 100 ml. of kerosene and 100 ml. of xylene (which has about the same solvent properties as a mixture of crude oil and xylene) to which had been added 4 ml. of a 5 per cent xylene solution of Destabilizer A. The aqueous phase was separated and analyzed for calcium.

The solution so treated was in all cases found to contain the same amount of calcium, within experimental error, as the original solution. Apparently, at the dilution obtained in the extraction, the calcium sulfonate remains almost completely in the aqueous phase. Since the magnesium sulfonates are generally more water-soluble and less oil-soluble than the calcium sulfonates, it is concluded that magnesium also is left nearly completely in the aqueous phase.

Xylene is recommended as a diluent for the oil, since it has good solvent action on most petroleum, a low vapor pressure with consequent low fire and poison hazards, and a low specific gravity, a property which gives a larger specific gravity differential between the oil and water phases and thus permits faster and more complete settling out of the water. Benzene, toluene, or gasoline may be used if xylene is not available.

The efficiency of salt extraction by this method depends greatly on the agitation given to the mixture after addition of the water. The shaking time of 5 minutes given in the above procedure has been found sufficient to extract at least 95 per cent of the salt from even the most difficult samples. Usually, in the determination of the salt content of oils, extremely accurate analyses are not required, and some sacrifice may be made in accuracy in order to permit a more rapid determination. Within 5 per cent of the true salt content value is generally considered sufficiently accurate.

In order to determine the extent to which the efficiency of the extraction depends upon the time of agitation, analyses for total halogen were made on several crude oils, varying the time of agitation. The shaking was done by hand at the rate of from 150 to 200 shakes per minute. Halogen was determined by the Mohr method (1), with corrections for the blank being applied. Table I shows the results obtained on a

typical high salt content crude from Shuler, Ark. Very little increase in accuracy is obtained by shaking more than 5 minutes, but values nearly 15 per cent low may be obtained with only 3 minutes' agitation. This oil contained 0.4 per cent of emulsified brine and is considered difficult to analyze by other methods. Results are expressed in milligrams of sodium chloride per liter of crude.

In the petroleum industry, chloride contents of crude oils are often expressed as grams of sodium chloride per barrel (of 42 gallons) or as pounds of sodium chloride per 1000 barrels. The relations between these units and the metric units employed here are as follows:

$$\begin{aligned}\text{Grams per barrel (42 gallons)} &= \text{mg. per liter} \times 0.1590 \\ \text{Pounds per 1000 barrels} &= \text{mg. per liter} \times 0.3505\end{aligned}$$

Similar tests were made on an oil of low salt content from Oklahoma. This oil contained 0.2 per cent of dispersed brine and is considered easy to extract by other methods. Table I also gives the results of these tests. With this oil, 3 minutes agitation gives satisfactory extraction.

These same oils were analyzed also by the U. O. P. method three extractions being made of each sample. Results of these analyses are given in Table II.

TABLE II. HALOGEN DETERMINED BY U. O. P. METHOD

	(Mg. of NaCl per liter of crude)					
	In Shuler Crude			In Oklahoma Crude		
	1	2	3	1	2	3
1st extraction	868	881	811	135	134	14
2nd extraction	77	86	120	8	8	..
3rd extraction	3	6	23	2	4	..
Total	948	973	954	145	146	14

In the case of the Shuler crude, the salt removed by three extractions using the U. O. P. method was 2 to 8 per cent below the maximum values and averaged less than the 5-minute values shown in Table I. With the Oklahoma oil, the value obtained after three extractions by the U. O. P. method agreed with those of Table I. However, with both oils, the first extractions by the U. O. P. method gave values 10 to 20 per cent below the maximum values obtained by the new method.

### Rapid Method

In routine analysis for halogens only, it has been found possible to modify the procedure described above to permit more rapid determinations. The volume of sample used in the procedure described below is in general too small to permit accurate analysis for cations. With many oils, the cation ratio, sodium to calcium to magnesium, remains constant over long periods of time and, after this ratio has been established, analysis for total halogens gives sufficient information for control work. In this procedure, a different destabilizer from that used in the longer procedure is employed—a mixture of isomeric compounds obtained by the acylation of polyhydroxy glycerides known under the trade name of Destabilizer B. The exact chemical structure of these compounds is not known. This material is much more effective than the sulfonic acid salts in flocculating the dispersed water droplets, but the coarse flocs formed do not easily coalesce under the influence of gravity, and for this reason cannot be used with the first method. In the centrifuging procedure, as employed in this rapid method, the coarse flocs are quickly coalesced and a clear aqueous layer is formed.

Into a 100-ml. standard A. S. T. M. oil centrifuge tube, pour 20 ml. of the crude oil and add 2 ml. of a 2 per cent xylene solution of Destabilizer B. Then add xylene to fill to the 50-ml. graduation mark. Shake for a few seconds and add 50 ml. of boiling chloride-free, distilled water. Stopper and shake vigorously for 2 or 3 minutes, and centrifuge for 1 minute. Pour the contents



of the tube into a small separatory funnel, draw off the aqueous layer, filter, and titrate an aliquot amount for halogens.

### Discussion of Rapid Method

If the graduations on the centrifuge tube are used to measure the volumes of oil and water added, results on a given oil may be expected to vary by 4 or 5 per cent at least, since volumes of fluid in the tube cannot be estimated to much closer than 1 ml. Again, one should correct for the decrease, on cooling, in the volume of water added. When the oil sample contains only small amounts of chloride, the experimental error may become greater than 5 per cent, because of the proportionately larger end-point error in the titration. Where the amount of salt present is small, the mercury nitrate method (2) of halogen determination is to be recommended in place of the Mohr method.

TABLE III. TOTAL HALOGEN BY RAPID METHOD

(Mg. of NaCl per liter of crude)	
Shuler Crude	Oklahoma Crude
975	133
1038	155
931	162
944	155

Table III shows the results obtained using this rapid method on samples of the two oils previously analyzed by the longer method. Graduations on the centrifuge tube were used to measure the volumes of oil, xylene, and water used. Halogen was determined by the Mohr method. These results may be compared with those given in Table I.

### Acknowledgment

The author is indebted to R. B. Perkins, Jr., of the Petroleum Rectifying Company for testing these two methods of analysis on a number of different crude oils.

### Summary

For quantitative extraction of inorganic salts from crude oils, it is desirable to employ a destabilizing agent which causes coalescence of the particles of emulsified brine present in the oil and prevents permanent emulsification of the extraction water.

A new method of extraction of inorganic salts from crude oil is presented. This method employs a mixture of ammonium salts of high molecular weight sulfonic acids as a destabilizing agent, and gives nearly quantitative removal of the salts in one extraction.

A rapid method of extraction is presented, which permits analyses for total halogens sufficiently accurate for control work. This method employs a destabilizer consisting of a mixture of isomeric compounds obtained by the acylation of polyhydroxy glycerides.

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# Approximate Specific Gravity Determination

## A Rapid Method for Use with Pecans and Similar Small Objects

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AT THE present time there seems to be no satisfactory method for the rapid determination of the approximate specific gravity of pecans and similar small objects. In determining the specific gravity of individual pecan nuts, it was found that gravimetric methods were slow and the apparatus described herein was constructed to facilitate more rapid measurements. It may be used for the determination of the approximate specific gravity of small objects whose specific gravity is less than unity, and which are unaffected by immersion in water or other liquids of the same density. The apparatus is simple and is easily and cheaply constructed.

### Method and Apparatus

The method involves weighing the object to 0.01 gram and subsequently measuring its buoyancy directly in distilled water at room temperature by the hydrometerlike apparatus shown on scale in Figure 1, *a*. It consists of a 50-ml. bulb, *A*, from a pet, to the lower end of which is sealed a bulb, *B*, to hold lead shot. To the upper end of bulb *A* a thin-walled glass tube of uniform 8-mm. outside diameter is sealed with a bend at *C*. A scale is constructed and fitted in the tube at *D*. A copper wire carriage, *E*, made of No. 20 gage wire, is fitted to the tube to depress the object, *F*, whose specific gravity is to be determined. A phosphor-bronze clip, *G*, with a sliding collar may be added to hold the object in the carriage. The instrument is weighted so that when it floats without load, the water level or zero point is at *H*. Its over-all length is 43 cm. and it may be used in a 1-liter graduated cylinder.

For the above instrument, the range of buoyancy determination is 8 grams with a scale calibrated for distilled water

at 20° C. to 0.1 gram which can be read to 0.05 gram. By altering the dimensions of the instrument and adjusting its sensitivity with an appropriate diameter of scale-tube, it can be adapted to measure the specific gravity of objects with other ranges of weight and volume. By adding the phosphor-bronze spring clip, *G*, to hold the object in the carriage and extending the scale upward, measurements of specific gravity of objects heavier than water may be made. Using a mixture of ligroin and carbon tetrachloride or some other suitable liquids having the density of water, the specific gravity of objects which would be affected by immersion in water may be obtained. The formulas for calculating the specific gravity are as follows:

$$\text{Specific gravity} = \frac{W}{V} = \frac{Wd}{W + B} \quad (1)$$

where *W* is the weight in grams, *V* the volume in ml., *B* the buoyancy in grams, and *d* the density of the liquid used.

If the density of the liquid is unity, *d* = 1, and the formula reduces to

$$\text{Specific gravity} = \frac{W}{W + B} \quad (2)$$

Since the specific gravity determinations are approximate, no correction is made for the density of distilled water (0.998, 1) at room temperature (20° C.) and Formula 2 is used in the calculations. For objects heavier than water Formula 2 still



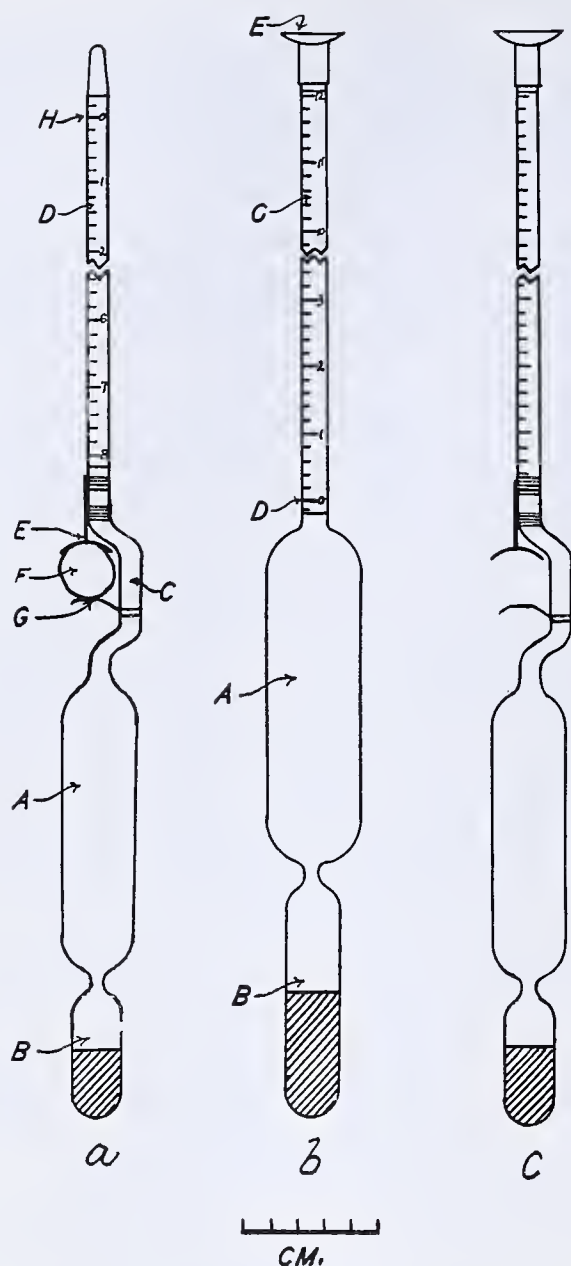


FIGURE 1. APPARATUS FOR BUOYANCY AND WEIGHT DETERMINATIONS

holds; the "buoyancy" is negative and would therefore be subtracted from the weight.

In practice it is well to have the graduation marks on the scale extend a little beyond the zero mark. In this way slight deviations of the instrument from the zero point can be measured and a correction applied to the readings. The density of the water may be adjusted, if desired, by adding a suitable solute.

In Table I are given the specific gravities of a series of pecan nuts as determined by the above apparatus and by a more accurate gravimetric method. The weight range of the nuts was from 3.05 to 14.63 grams, the buoyancy from 0.50 to 8.20 grams, and the specific gravity from 0.33 to 0.96. An idea of the accuracy of the method is given by an inspection of the specific gravities as obtained by both methods. In only one instance (No. 3) did corresponding specific gravities differ by more than 0.01. Weighings to 0.01 gram can be made in about 1 minute, and with a little practice a buoyancy determination can be made in 30 seconds.

An apparatus for measuring the weights of the objects has also been developed. While it has only a slight advantage in speed over a balance weighing to 0.01 gram and is accurate to 0.05 gram, it also has the advantage of simplicity, cheapness,

and ease of construction. The apparatus is shown in Figure 1, *b*. It consists of a 100-ml. bulb, *A*, with a bulb, *B*, for lead shot. The tube, *C*, is 11 mm. in outside diameter and has a scale calibrated from 0 to 12 grams with 0.1-gram divisions. A carriage, *E*, is fitted to the top to hold the object, and the apparatus floats without load with the water level at *D*. The over-all length is 43 cm. and it may be used in a 1-liter cylinder.

In calibrating either apparatus, the stem is left open and the apparatus is temporarily weighted so that it floats with the water level near the base of the stem. A thin crayon mark is made on the stem at the water level. Then a 4- or 5-gram weight is attached to the upper end of the stem, the apparatus is allowed to come to equilibrium and a second crayon mark is made on the stem at the water level. The distance between the two marks is then measured. Since the weight required for this displacement of the stem is known, the displacement due to a weight of 1 gram can be calculated. From the data a scale is constructed and fitted in the stem with a little mucilage to prevent sliding. The apparatus is finally weighted so that the water level is at the zero point of the scale and the stem sealed shut. Care must be taken not to lose any glass in the sealing or alter the weight of the apparatus after the final weight adjustment has been made. For weighting, No. 6 lead shot have been found convenient, and some powdered sealing wax is poured in along with the shot. After the final weight adjustment, the weight bulb is heated gently until the wax just melts, and on cooling it holds the shot in place.

In Figure 2 is shown a nomogram derived from Formula 2 whereby specific gravity may be read directly without calculation. The weight is read off on the abscissa and the buoyancy on the left-hand ordinate. Through the origin (0, 0) and the point representing the weight and buoyancy, a straight line is drawn to intersect the right-hand ordinate, and the specific gravity is read off at the point of intersection. For convenience and rapidity of determination these lines may be drawn in as shown.

TABLE I. SPECIFIC GRAVITY OF PECAN NUTS

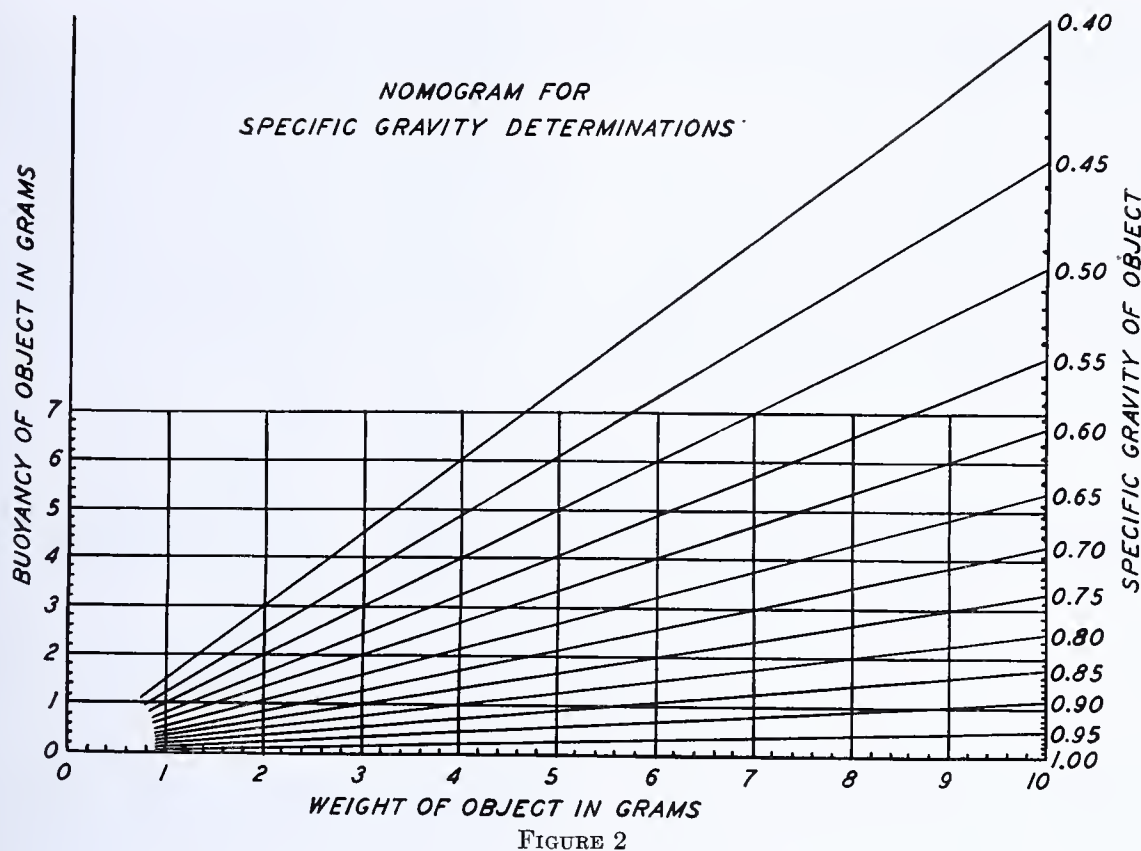
Nut No.	Weight of Nut Grams	Buoyancy of Nut Grams	Specific Gravity of Nut By apparatus	Specific Gravity of Nut By gravimetric method	Error in Specific Gravity Determination by Apparatus
1	10.95	1.30	0.894	0.899	-0.005
2	14.63	0.65	0.957	0.966	-0.009
3	12.65	0.50	0.962	0.973	-0.011
4	9.02	2.80	0.763	0.763	+0.000
5	9.15	2.50	0.785	0.781	+0.004
6	9.97	2.30	0.813	0.810	+0.003
7	8.31	3.30	0.716	0.710	+0.006
8	9.03	2.60	0.776	0.773	+0.003
9	8.70	2.25	0.795	0.791	+0.004
10	6.17	3.95	0.610	0.604	+0.006
11	4.71	2.45	0.658	0.653	+0.005
12	5.66	3.50	0.618	0.615	+0.003
13	4.76	2.45	0.660	0.655	+0.005
14	6.25	4.15	0.601	0.593	+0.008
15	4.17	4.60	0.475	0.472	+0.003
16	3.88	6.45	0.376	0.372	+0.004
17	5.79	4.20	0.580	0.575	+0.005
18	4.74	5.05	0.484	0.481	+0.003
19	3.20	3.65	0.467	0.466	+0.001
20	4.42	5.65	0.439	0.437	+0.002
21	4.67	6.00	0.438	0.433	+0.005
22	4.13	4.00	0.508	0.504	+0.004
23	3.05	4.40	0.409	0.407	+0.002
24	4.02	8.20	0.329	0.326	+0.003

The instrument can be adapted to different ranges of weights, and for certain restricted ranges of weight and volume the buoyancy and weight apparatus can be combined into a single instrument as shown in Figure 1, *c*, where buoyancy is read up and down and weights are read upward from a centrally located zero point on the scale.

### Summary

Apparatus has been developed for the rapid determination of approximate specific gravity of small objects of restricted ranges of weight and density. The method involves weighing the object directly and subsequently determining its buoyancy by means of a hydrometerlike apparatus. From these data





the specific gravity is calculated. For objects with a weight range from 3 to 15 grams, a buoyancy from 1 to 8 grams, and specific gravities from 0.33 to 0.95, a comparison of the method with a more accurate gravimetric method indicates it is accurate to within 0.01 specific gravity. In this range a complete determination can be made in 1.5 minutes. For more approximate work a hydrometerlike apparatus for weighing and a nomogram to eliminate calculations are described.

While restricted to a given range, the instrument may be adapted to various specific gravity ranges.

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RECEIVED January 24, 1938.

## Quantitative Spectrographic Analysis

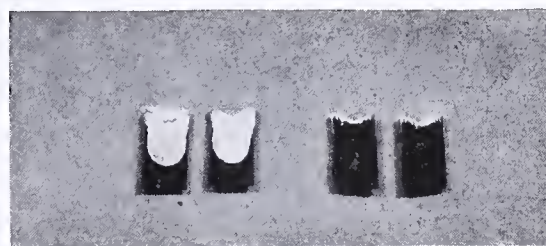
### Treatment of Graphite Electrodes for Evaporation of Aqueous Solutions

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ALTHOUGH methods of direct excitation of emission spectra of substances in an aqueous solution have been developed for use in spectrographic analysis, it is often more convenient to evaporate a known amount of a solution, or its concentrate, directly in a shallow cup in one end of an electrode and then excite the spectrum of the residue by using the electrode in the light source. When an evaporation is made in the cup of a plain graphite electrode there is always some penetration of the solution into the graphite. The depth of this penetration, which determines the distribution of the residue in the graphite electrode, is a variable that depends on the kind and concentration of the solution, the rate of evaporation, and the nature of the graphite. Since careful quantitative work of this kind usually necessitates controlled penetration of solutions into the electrodes, a method of testing and a method of reducing this penetration are presented here.

A solution for testing the penetration was made by dissolving 10 grams of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in sufficient 25 per cent nitric acid to make 1 liter of solution. The electrodes used in the tests were 1.56-cm. (0.625-inch) lengths of 0.78-cm. (0.313-inch)

rounds of spectrographic graphite. A conical shaped cup was drilled in one end of each of the electrodes. The electrodes were heated to about  $1500^\circ\text{C}$ ., cooled, treated with materials for reducing the penetration, and then placed in holes in a copper block. The temperature of this block was maintained at a few degrees above  $100^\circ\text{C}$ . during the dropwise evaporation of 0.5 cc. of the test solution on each electrode. Following the evaporations, which required about 30 minutes, the dried calcium nitrate



A                      B

FIGURE 1. PHOTOGRAPH OF ELECTRODES WITH CALCIUM OXIDE RESIDUES

A. Plain graphite  
B. Graphite treated with paraffin



residues were scraped from the cups. Each electrode was then sawed in two lengthwise and the halves were heated to a high temperature with an oxygen-gas flame. This process formed calcium oxide in the regions where the depositions of calcium nitrate had been made.

Representative penetrations into plain graphite are shown in Figure 1, A, where the calcium oxide residues extend far down into the electrodes. The electrodes shown in Figure 1, B, were each treated with 0.04 cc. of melted paraffin before the solution was evaporated. In the latter case very little penetration took place; therefore most of the calcium nitrate was deposited in the cups. Of the materials tried, paraffin and heavy mineral oil were found to be most effective in re-

ducing the penetration of the solution, resisting change by chemical action, and facilitating the vaporization process.

The oil film that is produced on the graphite particles by treatment with paraffin or with mineral oil prevents wetting of the graphite by the water solution. The proper amount of paraffin or oil does not completely close the pores in the electrode; therefore the vapors from the solution can pass through the electrode. This allows rapid vaporization to take place from the bottom of the drop of solution without spattering. After a solution has been evaporated to dryness, the paraffin or oil can be driven out of the electrode by heat.

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## Coprecipitation and pH Value in Precipitations with 8-Hydroxyquinoline

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The separation of metals by use of 8-hydroxyquinoline requires careful control of the pH value during precipitation. If zinc is precipitated in the presence of magnesium, serious coprecipitation occurs unless the pH value is kept at least two pH units lower than the value at which magnesium alone is precipitated. The separation of ferric iron and aluminum is possible within narrow limits of hydrogen-ion concentration.

THE importance of adjusting the pH value of solutions in which metals are to be precipitated with 8-hydroxyquinoline was recognized by Berg (1, 2). Goto (6, 7, 8) has reported the limiting pH values for complete precipitation of a number of metals, but in each case precipitation was made from a solution of the pure salt. Similar studies have been made by Fleck and Ward (4, 5), who made precipitations from solutions of the pure salts and predicted from their results that certain separations should be possible.

This study was undertaken because it seemed probable that in actual separations the pH range in which satisfactory precipitations could be made would be much more limited than that which was indicated in the experiments with solutions containing a single metal. This was found to be true in the precipitation of zinc in the presence of magnesium and in the separation of iron and aluminum. When zinc is precipitated with 8-hydroxyquinoline in the presence of magnesium, a partial precipitation of magnesium begins at pH 5.5. Under the same conditions precipitation of magnesium alone begins at pH 7.5, as reported by Fleck and Ward (5). In the case of ferric iron and aluminum, good separations were obtained only between pH 3.5 and 4.0.

### Experimental

**ZINC AND MAGNESIUM.** Solutions of zinc sulfate and magnesium sulfate were prepared and standardized by precipitation with ammonium phosphate and also with 8-hydroxyquinoline. The pH values were determined with a Leeds & Northrup glass electrode which was used with a vacuum-tube amplifying circuit similar to that of Ellis and Kiehl (3). The magnesium sulfate solution contained 1.2200 grams of magnesium per liter and the zinc sulfate solution contained 5.0976 grams of zinc per liter.

Solutions for analysis were prepared by mixing 10 ml. of each standard solution with 100 ml. of water, adding 15 ml. of ammonium acetate solution (0.2 gram per ml.) as a buffer, and using acetic acid, hydrochloric acid, or sodium hydroxide to adjust the solution to the desired pH value. Since the solution becomes more acid during precipitation, the values finally recorded (Figure 1) were determined on the filtrates at room temperature.

The solution was heated to 60° to 70° C. and 8-hydroxyquinoline, 2 per cent in 1 *N* acetic acid, was added, 20 per cent in excess of the volume required to precipitate the metal. The precipitate was digested for 30 minutes on a steam bath with stirring and allowed to settle for 5 minutes before filtration through a porcelain filtering crucible. After washing with hot water until free from sulfates it was dried in the oven for 3 hours at 130° C. and weighed as the anhydrous compound. The results are shown in

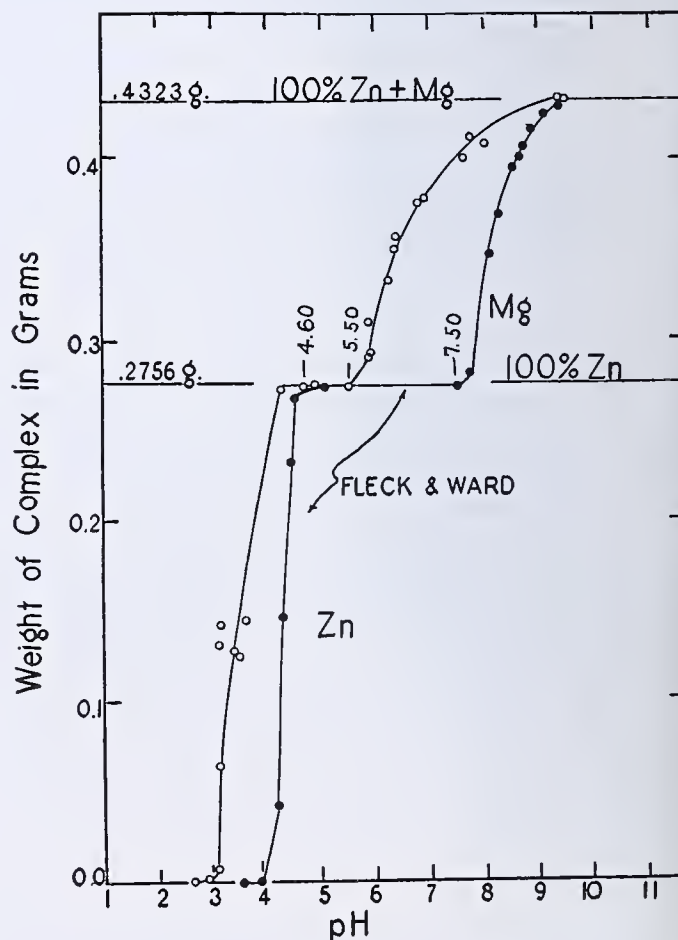


FIGURE 1



Figure 1, in which the curve of Fleck and Ward is reproduced for comparison. Since they used slightly more concentrated solutions, in order to make the results comparable their data have been recalculated, so that complete precipitation is represented by the same weight of precipitate as from the authors' standard solutions. Zinc is completely precipitated between pH 4.6 and 9.3 and coprecipitation of magnesium with zinc begins at 2 pH units lower than indicated on the curve by Fleck and Ward for the beginning of the precipitation of magnesium.

**IRON AND ALUMINUM.** Standard solutions of iron and aluminum were prepared and found to contain, respectively, 0.9540 gram of iron and 0.6972 gram of aluminum per liter. The analyses were made on mixtures, each of which contained 25 ml. of each solution with 3 grams of ammonium acetate, 25 ml. of 8 per cent tartaric acid, and enough water to make the volume 150 ml. The pH of the solution was adjusted to the desired value by adding hydrochloric acid or sodium hydroxide. Preliminary measurements of the pH value were made before the addition of the 8-hydroxyquinoline, but the values shown in Figure 2 were made on the filtrates at room temperature. The precipitation of the iron required 12 ml. of 2 per cent hydroxyquinoline solution. After the addition of the precipitant and the adjustment of the pH value, the solutions were heated over the steam bath to 85° to 90° C. for 25 minutes, then allowed to settle for 5 minutes before filtration. Between pH 3.45 and 4.00 the iron was found to be precipitated completely and less than 0.1 mg. of aluminum was found in each precipitate.

### Coprecipitation

Experiments were made to determine the effect of changes in the concentration of aluminum on the weight of aluminum carried down with the iron compound. All precipitations were made at pH 4.10, at which value aluminum begins to precipitate with the iron compound but is not precipitated with 8-hydroxyquinoline in the absence of iron. Precipitation of the iron was made under the same conditions in each case,

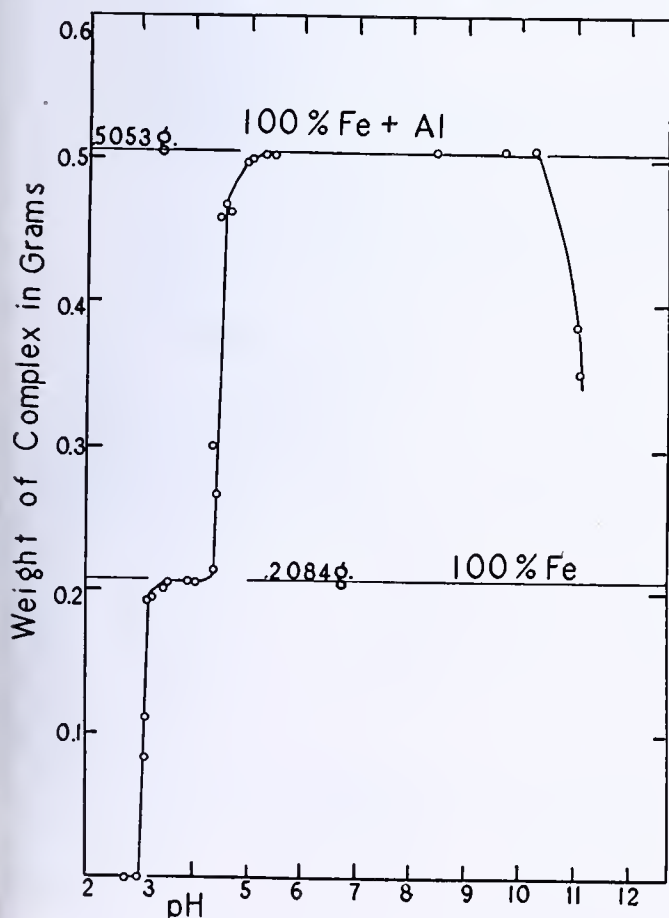


FIGURE 2

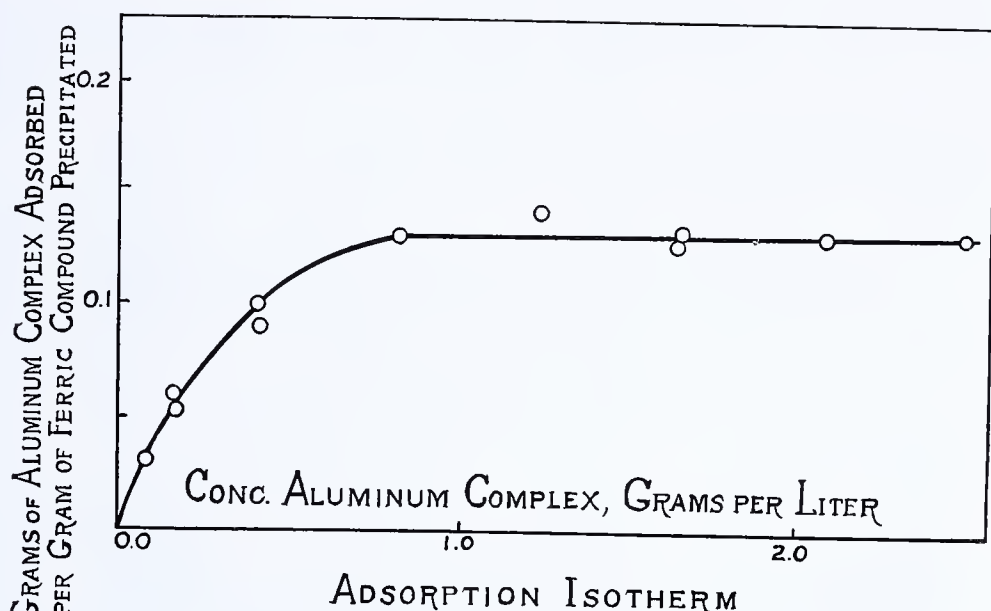


FIGURE 3

except that the concentration of aluminum, calculated as the aluminum hydroxyquinoline compound, was varied from 0.0823 to 2.4700 grams per liter. The same weight of ferric hydroxyquinoline compound, 0.0834 gram, was precipitated in each case. The analytical procedure was the same as described above and it is probable that equilibrium was not attained in all cases; nevertheless, if the weight of the aluminum complex carried down per gram of ferric compound is plotted against the weight of aluminum complex in solution, the result is a typical adsorption isotherm. After a tenfold increase in the concentration of the aluminum, the quantity adsorbed remains constant even if the concentration of aluminum is increased to 30 times its original value. The results are shown in Figure 3.

Similar experiments were made with magnesium and zinc at pH 5.9. The same quantity of zinc hydroxyquinoline compound, 0.2756 gram, was precipitated in the presence of varying concentrations of magnesium. The adsorption isotherm was found to hold for concentrations of magnesium, calculated as magnesium hydroxyquinoline, from 0.1 to 1.3 grams per liter. From 1.5 to 2.09 grams per liter the weight of magnesium compound which was carried down was nearly constant.

### Conclusions

Zinc and magnesium in concentrations given above can be separated by precipitating the zinc with 8-hydroxyquinoline, if the pH value of the solution is kept between 4.6 and 5.5.

Iron and aluminum can be separated if the pH value of the solution is kept between 3.5 and 4.0.

Coprecipitation of magnesium on zinc hydroxyquinoline at pH 5.95 and of aluminum on ferric hydroxyquinoline at pH 4.10 increases in accordance with Freundlich's adsorption equation until the concentrations reached certain values above which the quantity carried down remains constant. It is probable, therefore, that the coprecipitation is adsorption on the surface of the precipitate.

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- (7) *Ibid.*, 55, 1156 (1934).
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RECEIVED January 4, 1938. Based on work supported by a J. T. Baker Fellowship in Analytical Chemistry.

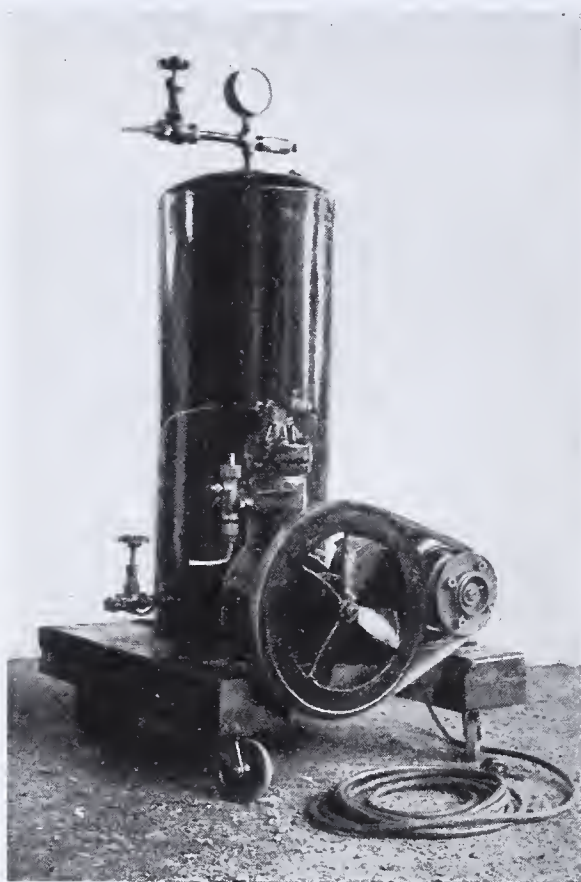


# A Small Portable Air Compressor Suitable for Laboratory Use

G. F. FLEMONS, Government Chemical Laboratory, Suva, Fiji

**T**HIS unit was evolved to meet the requirements for compressed air and partial vacuum called for in the normal laboratory. Its construction is simple and is well illustrated by the accompanying photograph.

**THE COMPRESSOR.** A very satisfactory compressor unit can be obtained from a refrigerator, the one illustrated having been removed from a discarded Kelvinator. It is fitted with a differential valve on the suction side, thus allowing any degree of vacuum to be employed without affecting the operation of the compression side by the restriction of the air intake.



AIR COMPRESSOR UNIT

**MOTOR.** The power of the motor will depend upon the output of the compressor and the amount of pressure required. Transmission is by means of a refrigerator belt, but the ordinary V-fan belting used on automobiles would prove equally satisfactory. Any convenient method of adjusting and maintaining the tension of the belt can be incorporated, but it has been found that a trouble-free system is obtained by pivoting the motor on one side of its base and allowing it to tension the belt by its own weight.

**PRESSURE CYLINDER.** The steel drum and fittings were taken from the benzoline-injection system of a Braun assay unit. Any suitable type of gas bottle could, however, be used. The air connections and needle-valve controls can be seen in the photograph. An adjustable blowout valve of the spring-loaded ball type provides for the maintenance of a fairly constant pressure in the cylinder. In the compressor unit described here, no electrical cutout was employed, as the mechanical device has proved remarkably satisfactory, maintaining a pressure of 30 pounds per square inch with a divergence of approximately 1 pound. An automatic electrically operated cutout of the diaphragm type could be in-

cluded, but it is recommended that in this case a mercury make and break should be employed, as this method will provide for trouble-free operation.

**GENERAL CONSTRUCTION.** The components are mounted, as shown, upon a strong baseboard fitted with swiveling rubber-tired wheels. This allows for ease of movement and also eliminates practically all vibration. The applications to which this unit can be put are varied and include the operation of the Hortvet cryoscope.

## Acknowledgment

The author is indebted to the Government Chemist for permission to publish.

RECEIVED September 1, 1937.

## A Reflux Bath Agitator for Low-Temperature Fractional Distillation Analysis Columns

J. W. TOOKE

Phillips Petroleum Company, Bartlesville, Okla.

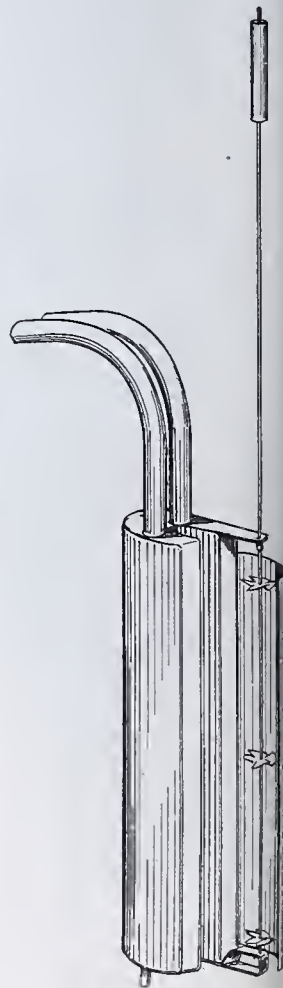
**T**HE usual methods of agitating the reflux bath of low-temperature fractional distillation analysis columns are not adequate in that too great a temperature difference exists between the top and bottom of the bath. This is especially true during and just after the introduction of liquid nitrogen into the expander.

In order to overcome this disadvantage the agitator herein described has been designed. The greatly increased circulation of the cooling bath liquid permits no perceptible temperature differential, thus ensuring better column control and sharper cuts between fractions. This apparatus also reduces vapor hazards to a minimum.

To a standard liquid nitrogen evaporator are soldered two bearings, one at the top and one at the bottom as illustrated. These bearings carry a 1-mm. steel shaft to which have been soldered three down-pitch impellers 5 to 7 mm. in diameter, made of thin sheet metal. The shaft and impellers are protected by a quarter-circular, thin sheet-metal shield, which also serves to hold the apparatus snug within the bath.

Motive power is supplied by a small induction-type nonsparking motor or air turbine, neither of which produces an appreciable vibration.

RECEIVED March 3, 1938.





# Modern

# Laboratories



(Left) BALL MILLS SUPPLEMENT STONE AND ROLLER MILLS IN GRINDING INKS, PAINTS, AND ENAMELS

(Center) CLEANING MILL TO PREVENT CONTAMINATION OF SAMPLES

(Right) SCHOPPER DETRITION MACHINE USED TO STUDY EFFECTS OF ROLLING PRESSURE ON RUBBER SAMPLES

## Colloidal Carbon Research Laboratory of Columbian Carbon Company

### Editorial Note

This new laboratory is unusually well equipped with testing apparatus selected with reference to problems in the production and use of colloidal carbon. It is unique in its effect on consumer industries and the influence exercised to a striking degree on the attitude of those using colloidal carbon toward research. In addition to the direct results of the research conducted in the laboratory, it has been responsible for the initiation of research elsewhere, and, indeed, for the establishment of new research centers.

COLUMBIAN CARBON'S new carbon research laboratory was designed with two primary purposes in mind: facility in conducting research on colloidal carbon and the variety of products utilizing it, and conferences with representatives of industries using the product. This duality of purpose has been carried through the entire layout in such a

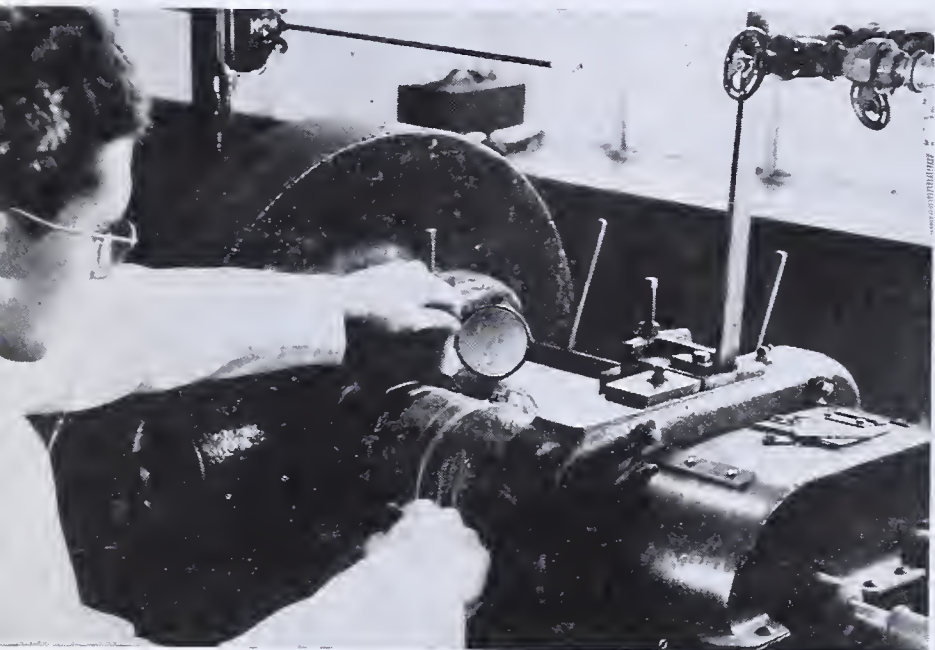
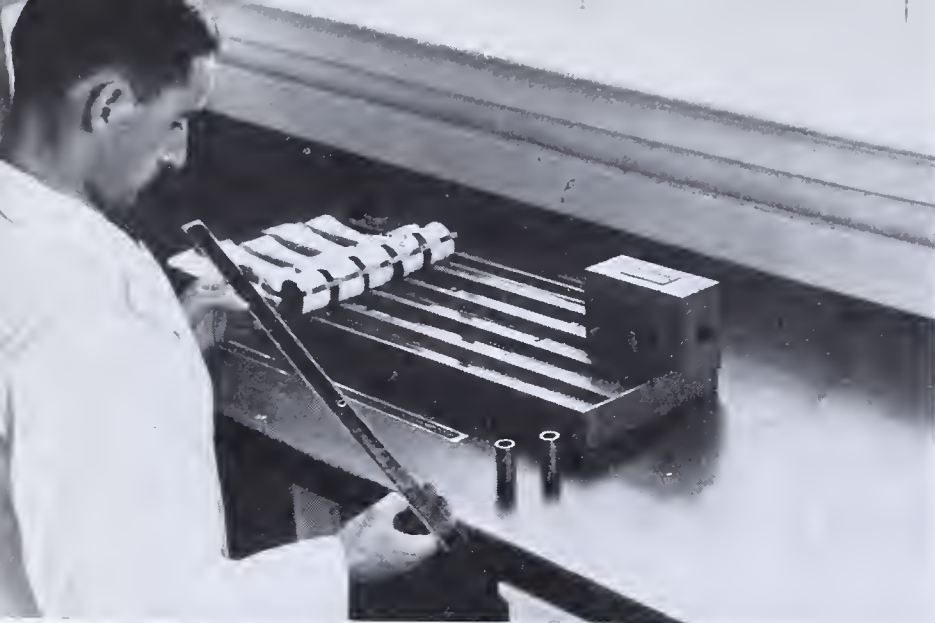
way that work under way is uninterrupted by visits of interested outsiders. On the contrary, equipment and technique have been developed to the point where visitors are able to learn much of value in their own work from the activities in progress in this four-story and basement building at 214-44th St., Brooklyn, N. Y.

Already impetus given to research by consumers of carbon shows the value of this plan and augurs well that indirect accomplishments will be added to direct results from work done here.

Important in the plan of this laboratory is its self-sufficiency. No plant surrounds it to interrupt its work with extraneous problems. Remote from colloidal carbon manufacture, the laboratory is equipped to begin at the beginning by making, if desired, its own carbons and to carry these through to the ultimate fate of products made with them.

Colloidal carbon manufacture is provided for in a pilot plant in which gas composition, flame character, placing of collecting channels, and other factors can be varied at will for study. Remote from a source of natural gas, the burners





in this pilot plant can be supplied with city gas, modified or replaced by propane, butane, pentane, or other hydrocarbons at will. Output is, of course, small—about 40 pounds per day—but the operation closely duplicates field conditions under more flexible control.

Quite as remarkable as the fact of manufacture of colloidal carbon in a populous city is the cleanliness of the operation of this pilot unit and the entire laboratory when the character of the material handled is considered. As a matter of fact, the pilot carbon plant opens directly off the reception room and museum, which occupies the ground floor of the building, yet so successful is the arrangement of draft and ventilation that no dust can fly from one to the other.

A further important factor in cleanliness is the provision of a common weighing and mixing room, under suction, in which all colloidal carbon is handled until mixed with other materials to prevent dusting. From this room, located in the middle of the second floor of the building, experimental batches of material move one way to the rubber processing room and in the opposite direction to the paint and ink milling room. This mixing and weighing room is also located directly on the freight elevator which brings in supplies from the delivery platform or from the storage space in the basement.

From this point of batching, samples follow two lines, one through the rubber department up the rear of the building and the other through the paint and ink department up the front.

### Rubber Department

On the second floor, adjacent to the mixing and weighing room, is a special small room containing the rubber mixing rolls and a Banbury mixer where rubber batches are processed. From here, batches are taken to calenders and sheeting rolls and thence to three steam vulcanizing presses. One press is operated by hand for special work, a larger one is hydraulically actuated, and an autoclave provides for open steam cures. In the presses standard test specimens are cured and thence are taken to the testing laboratory on the third floor.

In the rubber laboratory, modern static testing machines—the Scott tester for tensile strength, elongation and rupture the Goodrich plastometer, T-50 test equipment (U. S. Rubber General Laboratories), oxygen and air aging bombs—are supplemented by an important and growing group of special apparatus for dynamic testing. Three abrasion machines of entirely different types (du Pont-Grasselli, U. S. Rubber, and Goodyear angle abrader) give three independent checks on abrasion resistance, the secret of longer tire mileage. The Schopper elastometer and the Goodyear-Healey rebound pendulum check rebound. The Schopper detrition machine and the de Mattia flexing machine test rubber under dynamic conditions. Some of these are modified for greater

### (Upper) DRYOGRAPH TO TEST DRYING OF PAINTS, LACQUERS, INKS, AND ENAMELS

A film of definite thickness is spread on the metal strip. The canton flannel strip, unrolled at very slow uniform speed, sticks to the film until it dries.

### (Second from Top) ROLLS FOR COMPOUNDING RUBBER TEST MIXES

### (Third from Top) DU PONT-GRASSELLI AND U. S. RUBBER ABRASION MACHINES FOR TESTING RUBBER SAMPLES

### (Bottom) MUSEUM OF PRODUCTS MADE WITH COLLOIDAL CARBON, IN CONFERENCE ROOM ON GROUND FLOOR OF LABORATORY



convenience or accuracy of measurement. The Goodyear-Healey rebound pendulum has been improved by the addition of a mercury electric contact for reading rebound more accurately than can be done using pawls to hold the pendulum at the top of the swing, and by the adoption of a newly designed pendulum arm to avoid vibration and hence give more exact results. The modified de Mattia flexing machine is now equipped to test samples in air or any desired gas under conditions of temperature, humidity, or composition variable at will.

Unique in the testing of rubber is a newly perfected machine for measuring stress and strain in rubber under any desired conditions of elongation and cyclic application of force. This machine gives the life and fatigue characteristics of rubber under conditions of dynamic stretch. Rubber samples in the form of annular rings are stretched between two horizontal cylinders, arranged to rotate about their axes. One of these is connected to the crank of a motor-driven fly wheel and the other, to a balanced pendulum so constructed as to be out of phase with the impulses of the crank and to indicate the average pull on the sample. Elongation of the sample can be varied at will and its fatigue characteristics determined under any desired conditions of elongation and high-speed cyclic stroke.

### Paint and Ink Department

The course of paint and ink batches is similar. On the second floor are set the various mills for grinding them to complete dispersion. A dough mixer makes heavy pastes. Steel mills, buhr stone mills, ball mills, and roller mills, chosen according to results desired, complete the grinding. After dispersion, samples are taken to the third-floor laboratory for test. Included in its equipment are the dryograph for measuring drying time, flow-measuring devices, tacketers, viscometers, a color-matching room, and a spray painting booth for practical spray tests. The color-matching room, which is painted jet black inside and hung with black velvet curtains, is provided with a variety of lights to emphasize ultraviolet, infrared, or any desired part of the visible spectrum for comparison and test purposes.

On the third floor, too, are located the laboratory offices situated between the two testing laboratories. Here reports are prepared, work is discussed and planned, and the business of the laboratory is handled.

On the fourth floor is the chemical laboratory for chemical, distinct from physical, testing of raw materials and test samples. Its equipment is modern in every respect and includes three standard pH electrometers in addition to the more usual analytical and research apparatus.

Part of the fourth floor is also reserved for future expansion, for pilot-plant development, and for storage of the many test samples made in the laboratory.

### (Upper) ABRASION MACHINES FOR TESTING WEARING QUALITIES OF RUBBER

U. S. Rubber (left) and Goodyear angle abraders.

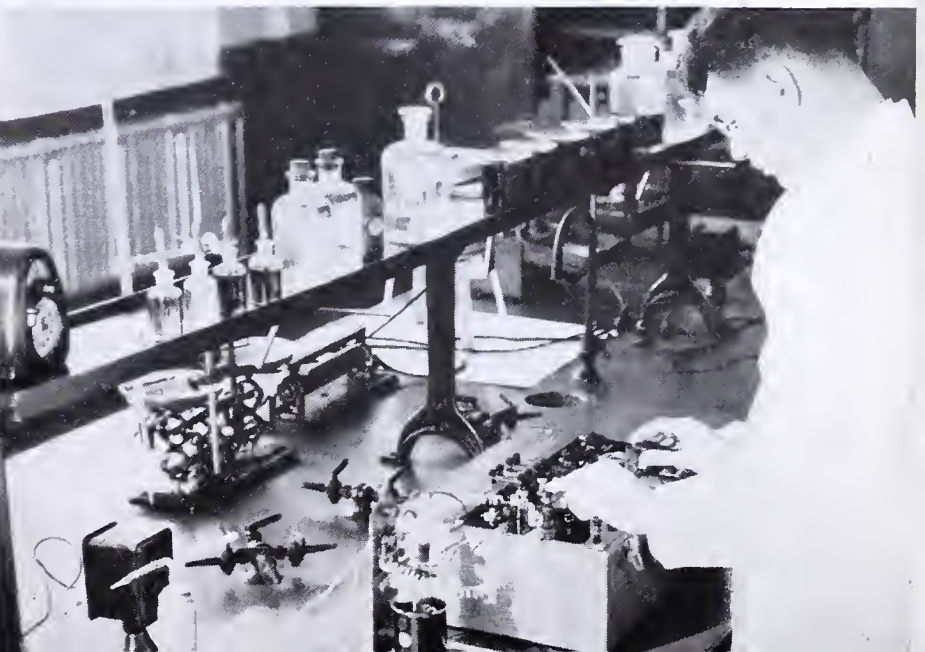
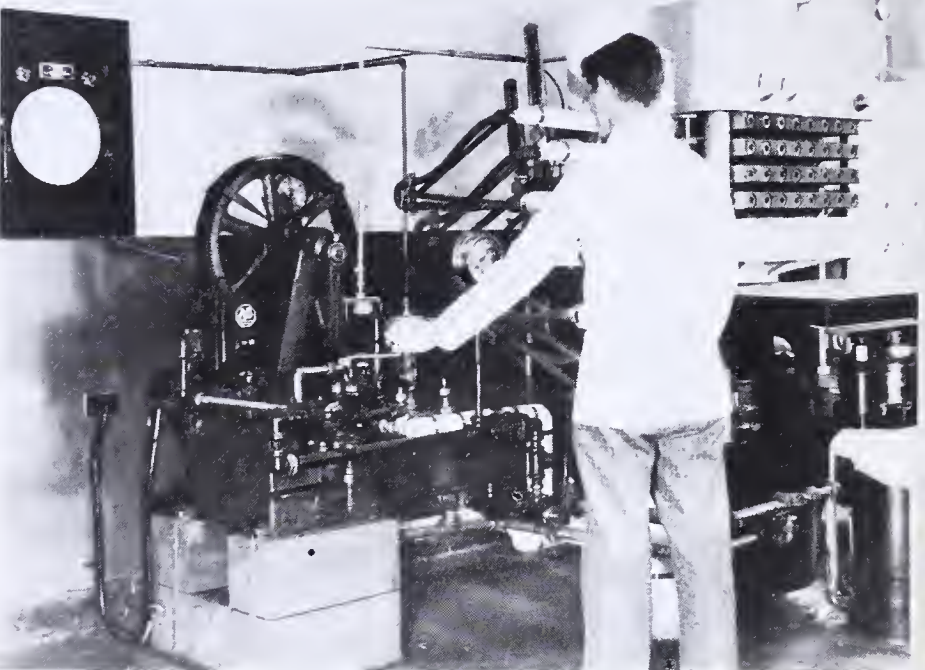
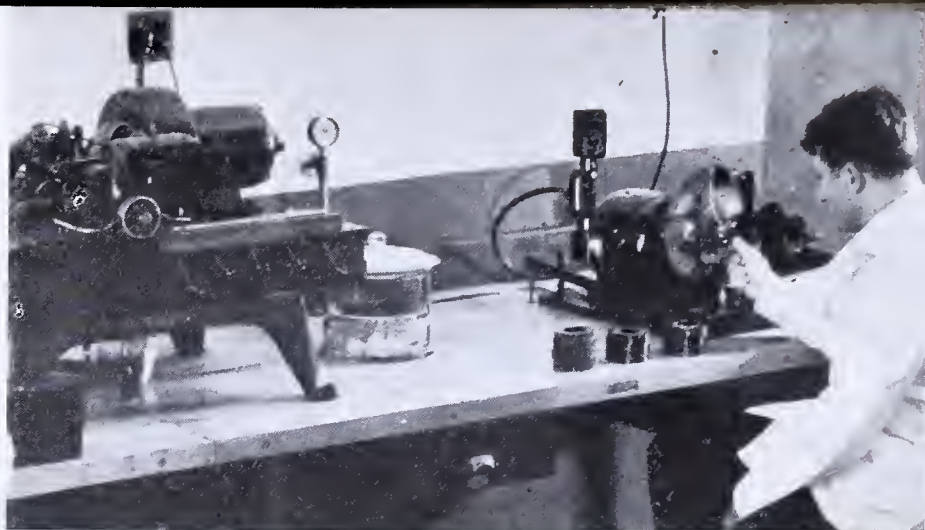
### (Second from Top) ABRASION MACHINES FOR TESTING RUBBER SAMPLES

Pont-Grasselli (left) and U. S. Rubber and Goodyear angle abrader (right)

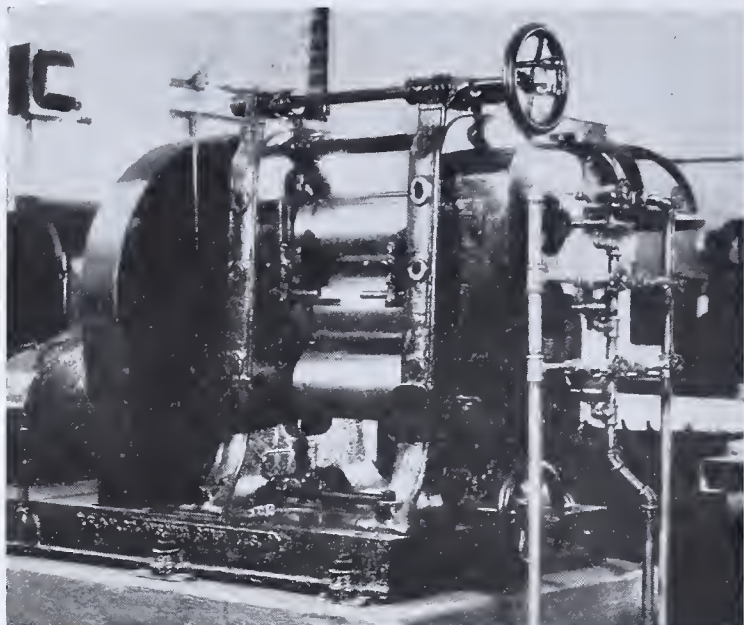
### (Third from Top) STEAM-HEATED HYDRAULIC PRESS FOR VULCANIZING RUBBER TEST SAMPLES

### (Bottom) DETERMINATION OF HYDROGEN-ION CONCENTRATION

Hydrogen-ion concentration is important in the dispersion and other characteristics of colloidal carbon in various media. In addition to the Leeds & Northrup instrument shown in operation, the laboratory is equipped with Coleman and Beckmann instruments.



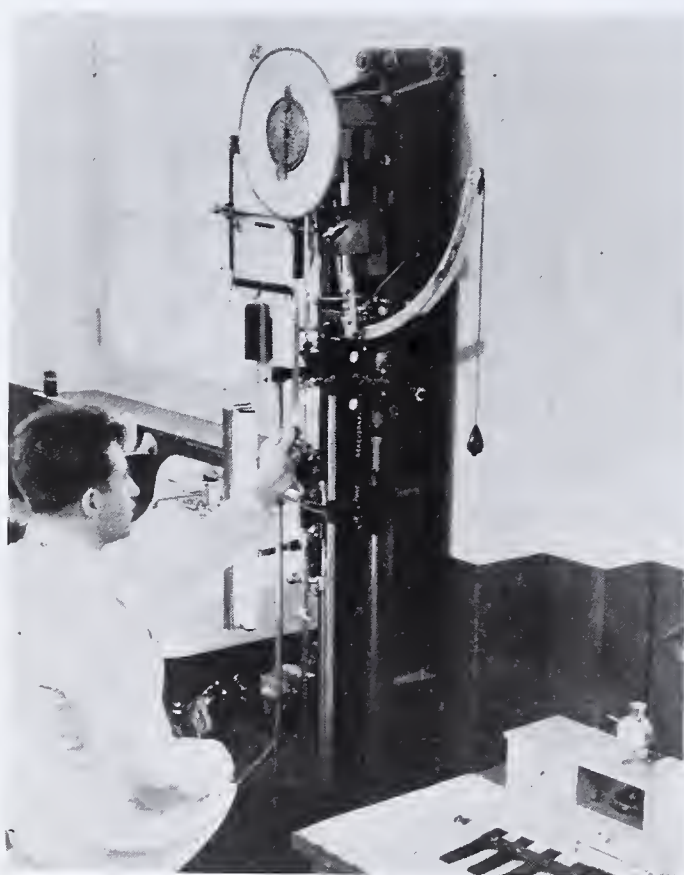




HEAVY CALENDER ROLLS USED FOR MILLING RUBBER DOUGHS

### Conference Room and Museum

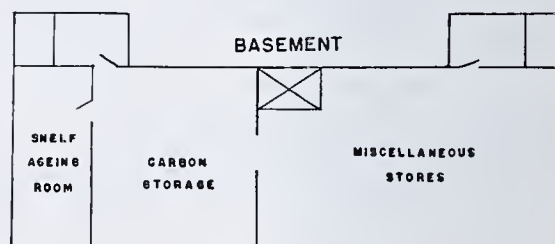
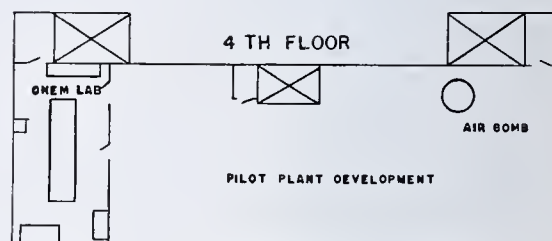
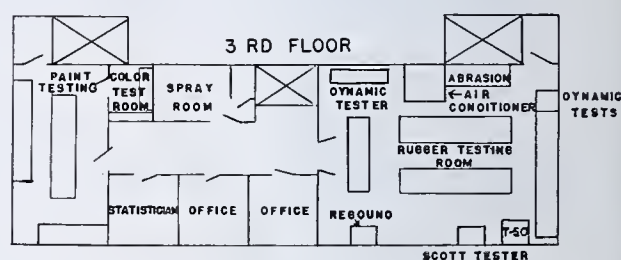
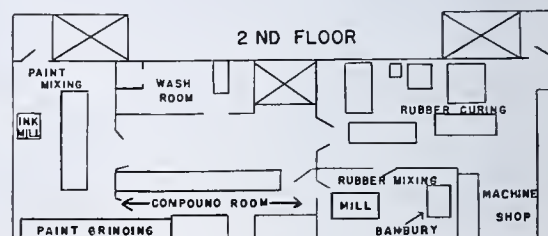
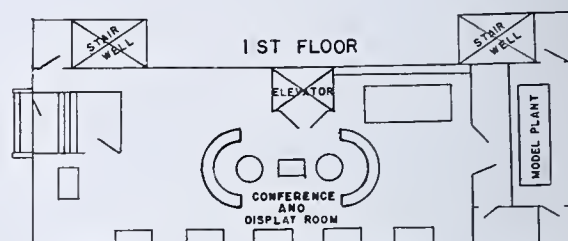
The character of the laboratory, its purposes, and the high caliber of the work to be expected from it are immediately impressed upon the visitor who enters the reception room on the ground floor. This large room (30 by 70 feet) is tastefully decorated in black and brown, colors made by the Columbian Carbon Company, with red leather-upholstered furniture for the comfort of guests. Here are held the industry conferences vital to the continuous shaping and reshaping of the research program to keep it in timely step with the needs of industry.



SCOTT TESTER FOR DETERMINING MODULUS OF ELASTICITY, TENSILE STRENGTH, ELONGATION, AND TEAR OF RUBBER

Here, too, are housed the laboratory's library and its museum of the many products made with colloidal carbon.

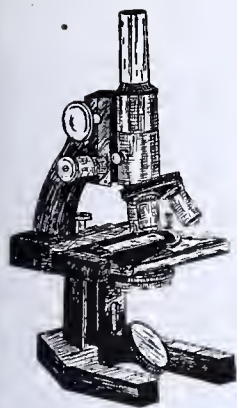
In keeping with this atmosphere, all laboratories carry out the black and brown color scheme and all workers in them are urged to neat accurate work by being clothed in white coats, despite the blackness of the product they handle.



### Purpose of Laboratory

The purpose of the laboratory is research on colloidal carbon, its production, its properties, and its applications. In some ways it partakes of the character of a service laboratory, although its primary purpose is research and not the solution of particular problems of particular purchasers. That function is performed specifically by the service laboratories of Binney & Smith Co., Columbian Carbon's pigment sales representative. The carbon research laboratory, on the other hand, explores new fields with the most modern technic and provides new facts as well as new methods valuable to consumers.





# Microchemistry

## Stabilization and Stability Tests of Cellulose Nitrates

E. BERL, G. RUEFF, AND CH. CARPENTER, Carnegie Institute of Technology, Pittsburgh, Pa.

THE stability of explosives, especially of cellulose nitrates, is of the greatest importance. Several experiments are described below which show how by different stabilization treatments the nitrogen content of cellulose nitrates, their viscosity, the ignition point, and their sulfuric acid content, expressed in percentage of bound sulfur trioxide are affected by different treatments.

Table I indicates that, in many cases, the nitrogen content is decreased by certain stabilization treatments, while in other cases it is increased. Experiments 6, 7, 9, 10, and 11 show an increase in the nitrogen content because unstable material with lower nitrogen content has been eliminated.

In most cases the viscosity of the cellulose nitrates is decreased. An increase in viscosity could be observed only in experiment 9, which shows that the treatment does not involve a degradation of the cellulose nitrate.

The ignition point is raised in all cases, but in experiments 1, 2, and 3 the increase is small and these treatments show practically no elimination of those substances which cause the instability. It is remarkable that for the treatments with distilled water (No. 1), with a weak base alone (No. 2), and with a weak acid alone (No. 3), the stabilization effect is rather poor. No. 4 is a combination of experiments 2 and 3, and gives a good stabilization effect. The highest ignition points are obtained in ex-

periments 6 and 9. It is remarkable that No. 5 also gives a rather high ignition point as compared with No. 3 because, with the addition of the wetting agent, the aqueous hydrochloric acid could wet the fiber.

Of great importance is the sulfuric acid content after the treatment, expressed in percentage of sulfur trioxide. The best result is obtained by experiment 4. Nos. 6, 7, 9, 10, and 11 show that the amount of bound or strongly adsorbed sulfuric acid is decreased below 0.1 per cent of sulfur trioxide in the material. (The sulfuric acid was determined by alkaline saponification of cellulose nitrate with sodium hydroxide free of sulfates, oxidation of the lower sulfur compounds with pure hydrogen peroxide, acidification, and precipitation of the sulfate with barium chloride. This method is described in Berl-Lunge, 6.)

### Stability Tests

In the literature many tests are described for determining the stability of cellulose nitrates and other explosives. They may be divided into qualitative, semiquantitative, and quantitative tests. Other tests are described which depend upon measuring the decrease in viscosity.

QUALITATIVE TESTS: Potassium iodide (1, 13); zinc iodide (15, 23, 30, 41). Diphenylamine (21, 27). *m*-Phenylenediamine (44).  $\alpha$ -Naphthylamine (17). Methyl violet (12, 36). Rosaniline (36). Lacmoid test at 108.5° C. (49); at 132° C. (7).

SEMIQUANTITATIVE TESTS: German test at 98° C. with phenylenediamine (29). pH determination (22, 32). Conductivity (32, 34). Spectroscopy (40). Ultraviolet light (8, 10). Silvered vessel test (24, 28, 43, 47, 50). Warm storage (31). Loss in weight (14, 37, 45, 48). Development of heat (2).

QUANTITATIVE TESTS: Will test (5, 39, 51). Bergmann-Junk test (3). Manometer method (9, 14, 16, 18, 20, 25, 26, 33, 35, 38, 40, 46, 53).

DECREASE IN VISCOSITY (4, 11, 19).

The following factors seem to be important for a scientific stabilization test:

1. Determination of the whole decomposition curve or an important part of it.
2. Use of only small amounts of explosives, so that an explosion is not dangerous.
3. The products of decomposition must remain in contact with the explosive, otherwise one gets a wrong picture.
4. The material to be tested should be in the same condition as is used later on. Therefore, the test should be made with cut or uncut cellulose nitrate, or with dense smokeless powder, depending on conditions of use. The action of the nitric oxides depends on the external conditions of the material.
5. The test has to be carried out in the presence of oxygen. The reoxidation of NO to N<sub>2</sub>O<sub>4</sub>.

TABLE I. EFFECT OF STABILIZATION TREATMENT

Treated Twice, Three Hours Each	Nitrogen		Logarithm of Relative Viscosity		Ignition Point (Corr.)		SO <sub>3</sub> Content	
	Before treat- ment %	After treat- ment %	Before treat- ment	After treat- ment	Before treat- ment ° C.	After treat- ment ° C.	Be- fore treat- ment %	After treat- ment %
1 Distilled H <sub>2</sub> O, 100° C.	12.6	12.55	1.7	1.65	135	141	0.68	0.60
2 0.02 N NaHCO <sub>3</sub> , H <sub>2</sub> O, 100° C.	13.3	13.15	2.3	1.85	136	140	0.63	0.56
3 0.1 N HCl, H <sub>2</sub> O, 100° C.	13.3	13.25	2.75	2.5	136	141	0.63	0.50
4 0.1 N HCl, 0.02 N NaHCO <sub>3</sub> , 100° C., 100 hours	13.47	13.36	1.32	0.54	157	185	0.31	None
5 0.1 N HCl + 2% wetting agent, H <sub>2</sub> O, 100° C.	12.7	12.65	1.7	1.7	156	186	0.68	0.26
6 50% CH <sub>3</sub> COOH + 2% CH <sub>3</sub> COO- Na, 105° C.	13.4	13.55	1.83	1.45	125	190	0.63	0.09
7 0.1 N H <sub>2</sub> SO <sub>4</sub> + CH <sub>3</sub> OH, 65° C.	13.3	13.5	2.3	2.1	136	188	0.63	0.08
8 0.1 N H <sub>2</sub> SO <sub>4</sub> + CH <sub>3</sub> OH, 101° C.	13.3	13.1	2.3	1.6	136	188	0.63	0.18
9 0.1 N HCl + CH <sub>3</sub> OH, 65° C.	13.4	13.55	1.8	1.93	125	190	0.63	0.04
10 0.1 N HCl + CH <sub>3</sub> OH, 101° C.	13.3	13.55	2.35	1.65	136	186	0.63	0.002
11 0.1 N H <sub>3</sub> PO <sub>4</sub> + CH <sub>3</sub> OH, 65° C.	12.6	12.8	1.7	1.55	136	186	0.67	0.03



(NO<sub>2</sub>) according to  $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$  is quicker than by the reactions  $\text{NO} + 2\text{HNO}_3 = 3\text{NO}_2 + \text{H}_2\text{O}$  and  $3\text{NO} = \text{NO}_2 + \text{N}_2\text{O}$ .

6. During the test the temperature has to be constant because of the high temperature coefficient of the reaction. The reaction speed doubles with a 5° C. increase in temperature.

7. The material must be completely dry, because water acts as a positive catalyst through saponification of the cellulose nitrate.

Several years ago Berl and Kunze (5) described a semimicrochemical stability test which is, in fact, an improved Will test (52). It used about one-fifth or one-tenth of the amount of cellulose nitrate used in the original Will test. The authors believe that both tests have certain weak points because they continuously remove the products of decomposition from the cellulose nitrate in decomposition and therefore give a somewhat inaccurate picture. Furthermore, they describe the decomposition only during and after a rather short time interval (see points 1 and 3 above).

### Glass-Feather Manometer

In the new stability test, advantageous use is made of the so-called glass-feather manometer described by Schaeffer and Treub (42). This is shown in Figure 1. (The glass-feather manometer is made by F. E. Donath, 22 Fourth St., Aspinwall, Pa.)

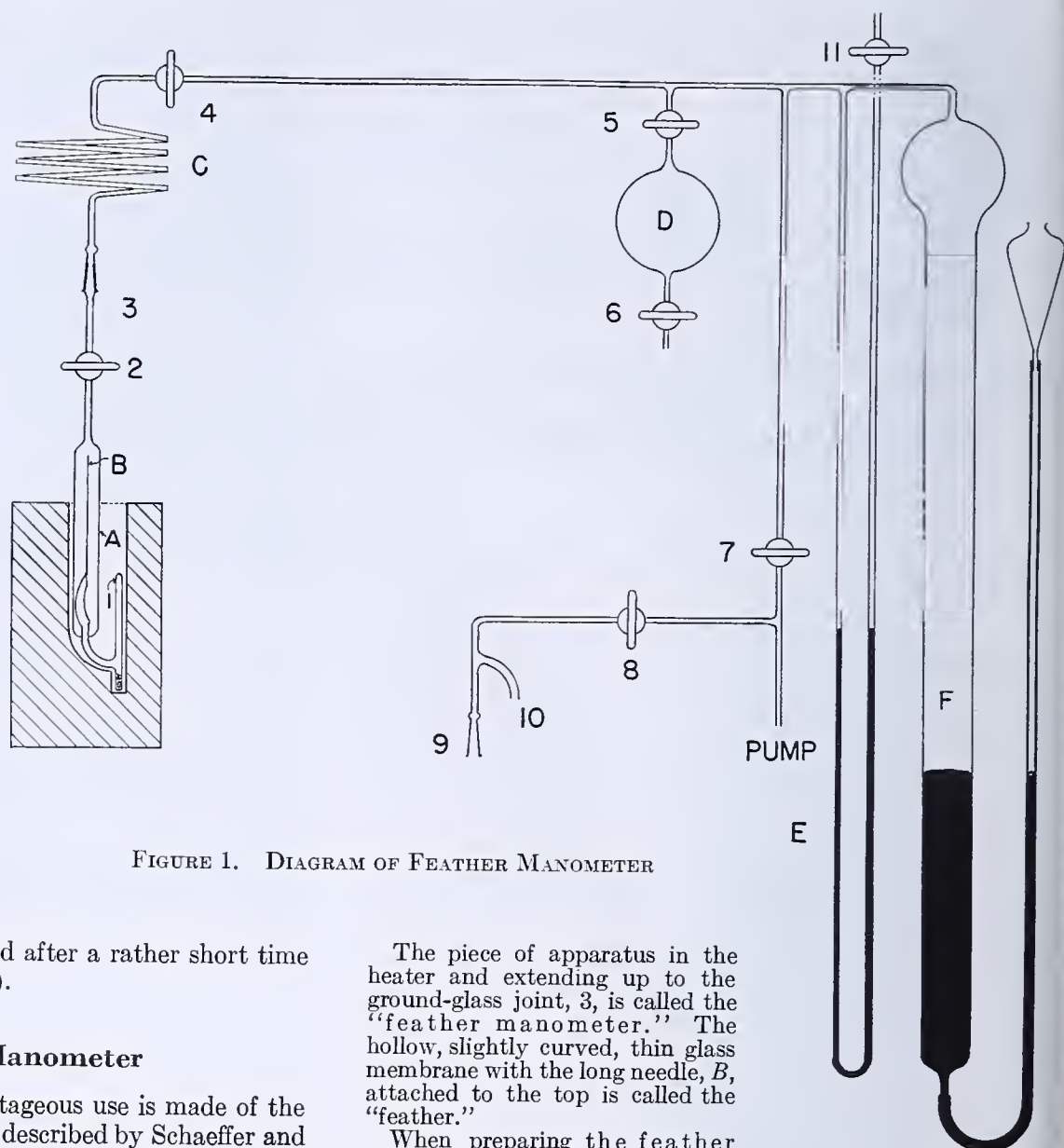


FIGURE 1. DIAGRAM OF FEATHER MANOMETER

The piece of apparatus in the heater and extending up to the ground-glass joint, 3, is called the "feather manometer." The hollow, slightly curved, thin glass membrane with the long needle, B, attached to the top is called the "feather."

When preparing the feather manometer for an experiment, tube 1 is open and extends up to the tip of the needle. The material to be tested is placed in the bottom of 1 and the feather manometer is then connected to the vacuum pump by means of the ground-glass joint, 9, and the tube, 10. Rubber pressure tubing is used to connect 1 and 10. When the necessary vacuum is produced in the feather manometer, 1 is sealed. The feather manometer is placed in the heater and connected to the mercury manometer system, which is then evacuated. The cross hairs of a rigidly mounted telescope are made to coincide with the tip of the needle. When pressure is produced inside the feather, the tip of the needle moves to the left. The pressure inside the feather can be determined at any time by adjusting the pressure outside the feather so that the tip of the needle again coincides with the cross hairs of the telescope. F is used to produce small changes in pressure outside the feather. Care must be used in handling the feather manometer, since the feather will stand only about 200 mm. Hg difference in pressure.

### Effect of Stabilization Treatments

For stability tests the authors use 5 or 50 mg. of cellulose nitrate in the absence or presence of air. Because of the very low weight of the explosives, if necessary, the rather high temperature of about 157° C. can be used without difficulty or danger.

A very important point in this and other tests is the preparation of the sample. The material to be investigated must be com-

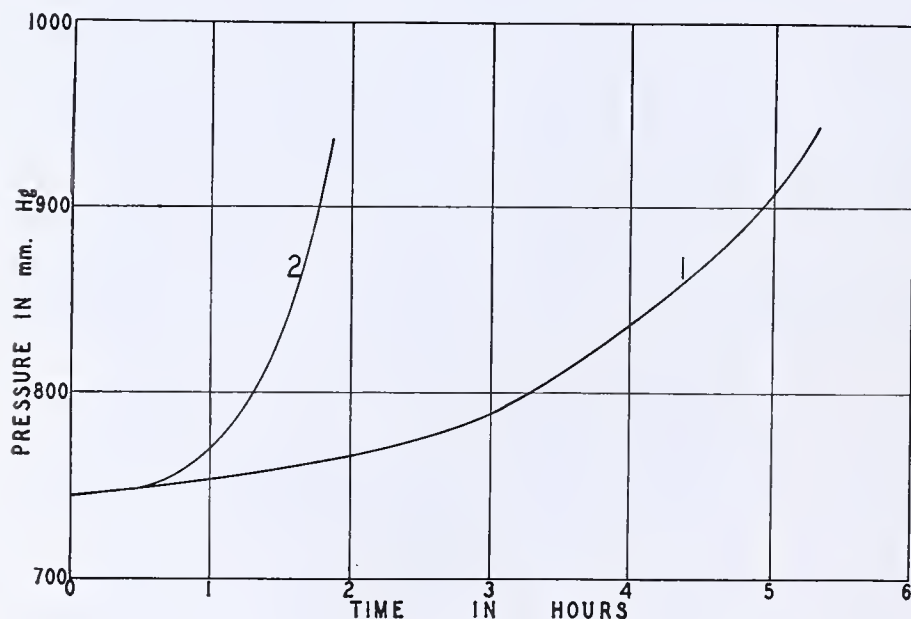


FIGURE 2. EFFECT OF TRACES OF MOISTURE ON DECOMPOSITION CURVES  
0.0500 gram of stabilized guncotton, dried over P<sub>2</sub>O<sub>5</sub>, 135° C. (uncorrected). 532 mm. air pressure at 25° C.

1. Moisture removed through heating at 100° C. under vacuum for 10 minutes or by vacuum for 16 hours at room temperature
2. Containing moisture adsorbed during manipulation



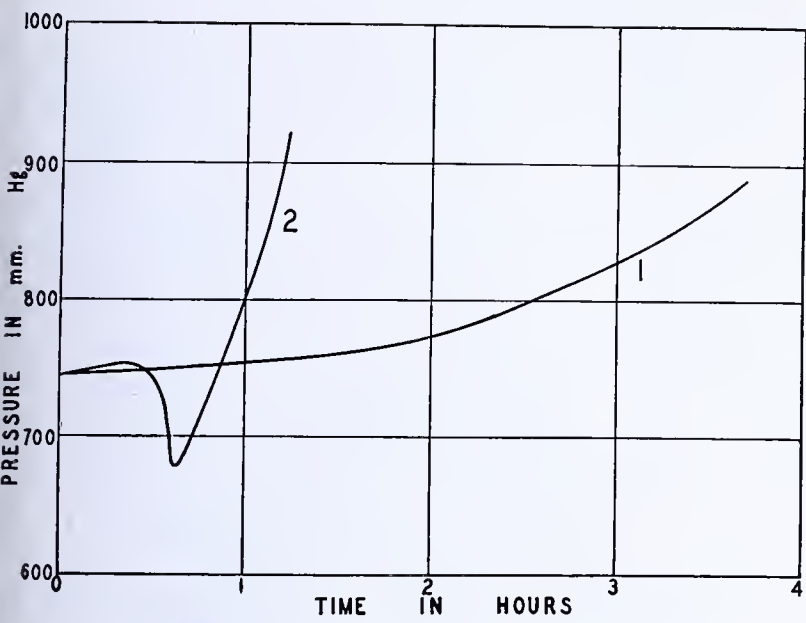


FIGURE 3. EFFECT OF TRACES OF MOISTURE ON DECOMPOSITION CURVES

0.0500 gram of nitrated linters, 11 per cent nitrogen, stabilized, dried over  $P_2O_5$ ,  $135^{\circ}C$ . (uncorrected). 532 mm. air pressure at  $25^{\circ}C$ .

1. Moisture removed through heating at  $100^{\circ}C$ . under vacuum for 10 minutes  
2. Containing moisture adsorbed during manipulation

pletely dry. Drying the sample over phosphorus pentoxide is not completely sufficient because, during the handling of this dry material, it quickly absorbs water from the atmosphere and gives inconsistent results. Figure 2 shows the difference in the decomposition curve of a guncotton if the material to be investigated is dried over phosphorus pentoxide and if this material, before sealing it in the glass-feather manometer, has been heated at  $100^{\circ}C$ . in a high vacuum for 10 minutes, or has been kept in high vacuum at room temperature for more than 16 hours. Figure 3 shows another experiment of this kind with a collodion wool which absorbs more water than guncotton.

From Figures 4 and 5 one can see that the method gives very reproducible results. The figures show the decomposition of different, completely stabilized samples, one investigated in vacuum at  $157^{\circ}C$ ., the other in air at  $135^{\circ}C$ .

Figure 6 shows the effect of washing unstabilized guncotton. Curve 2 shows the effect of washing with weak alkaline tap water and curve 1, with distilled water. The formation of a calcium salt of the sulfuric acid present as such, or in the form of a mixed ester, gives a higher stability.

Figure 7 shows the curves which were obtained in vacuum with unstabilized and stabilized guncotton at  $157^{\circ}C$ . (uncorrected).

Figure 8 shows a very interesting effect. The cellulose nitrate was decomposed in high vacuum. In spite of the absence of oxygen, a brown gas is observed which is converted afterwards into a colorless gas. The brown gas is nitrogen peroxide which plays an important role in the decomposition process. It is this nitrogen peroxide which acts as an autocatalyst. It is formed first by a slight saponification of the cellulose nitrate. The nitric acid formed oxidizes the organic part of the cellulose nitrate and is reduced to nitric oxide. Through destruction of the organic part of the nitric acid ester, new amounts of nitric acid are set free. They react with nitric oxide to form

$N_2O_4(NO_2)$ , which again burns parts of the organic substance and is reduced to nitric oxide. This reacts again with the newly formed nitric acid. This process goes on until practically all the organic substance is burned by nitrogen peroxide, which finally is converted into nitric oxide, nitrous oxide, and nitrogen. Then the atmosphere becomes clear. On opening the feather manometer, the brown color returns, showing that nitric oxide has been formed.

The nitrogen peroxide is the real catalyst which is responsible for the S-curve representing the autocatalytic decomposition reaction. This can be seen from Figure 9. The normal decomposition of cellulose nitrate took place. When about 50 per cent of the reaction had occurred, the gases were removed and the heating was continued. The break in the curve indicates that the observed pressure curve lies below the pressure curve expected, showing clearly the strong influence of the nitrogen peroxide.

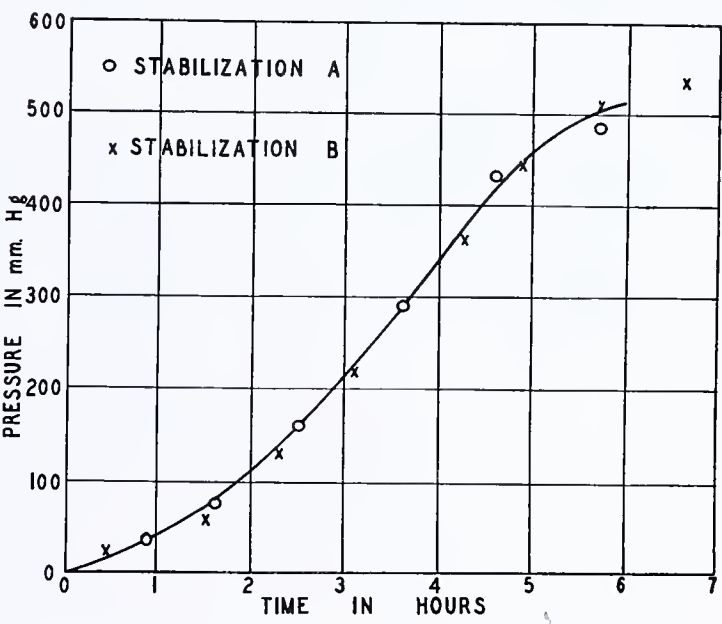


FIGURE 4. REPRODUCIBILITY OF DECOMPOSITION CURVES

0.0050 gram of guncotton nitrated with sulfuric and nitric acids and water.  $157^{\circ}C$ . (uncorrected), in vacuum

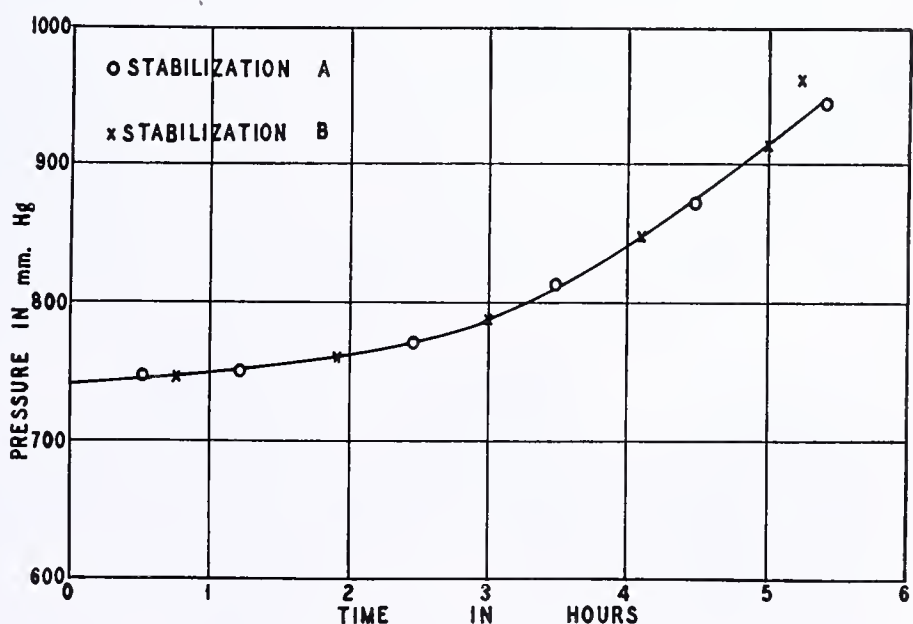


FIGURE 5. REPRODUCIBILITY OF DECOMPOSITION CURVES

0.0500 gram of guncotton nitrated with sulfuric and nitric acids and water.  $135^{\circ}C$ . 532 mm. air pressure at  $25^{\circ}C$ .



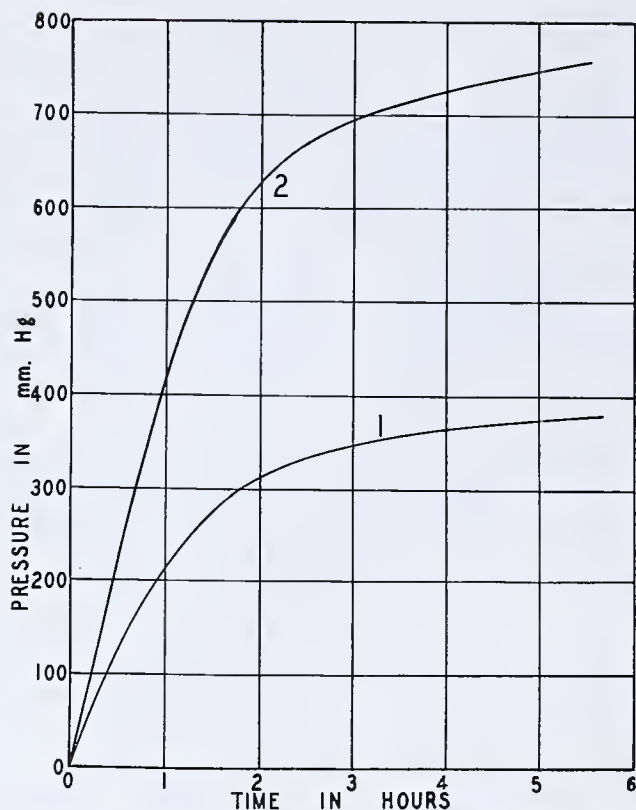


FIGURE 6. EFFECT OF WATER WASHES ON DECOMPOSITION CURVES OF UNSTABILIZED GUNCOTTON

0.0050 gram of guncotton nitrated with sulfuric and nitric acids and water.  $128^{\circ}\text{C.}$ , in vacuum

1. Washed in distilled water. Deflagrates at  $153^{\circ}\text{C.}$  Ash, 0.05 per cent. Residue dark, amorphous, water-soluble
2. Washed in tap water. Deflagrates at  $157^{\circ}\text{C.}$  Ash, 0.10 per cent. Residue brown, fibrous, partially water-soluble

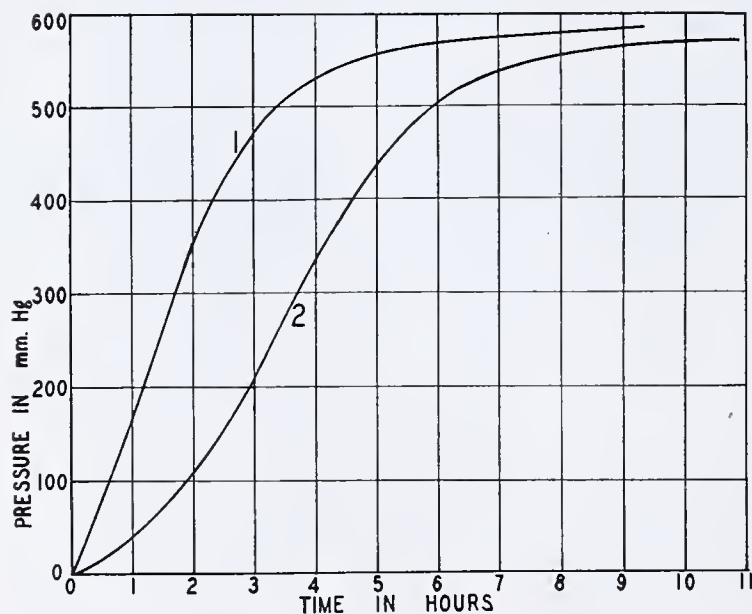


FIGURE 7. DECOMPOSITION CURVES

0.0050 gram of guncotton nitrated with sulfuric and nitric acids and water.  $157^{\circ}\text{C.}$  (uncorrected), in vacuum

1. Unstabilized, washed with tap water
2. Alcohol-stabilized

Figure 10 shows a decomposition curve for unstable and stable guncotton obtained with 5 mg. and at such an air pressure at room temperature that at  $135^{\circ}\text{C.}$  the air pressure was just 1 atmosphere. All these curves give an integration of the results. The differentials give a somewhat clearer picture. Figure 11 indicates the pressure differences which occur during the same time intervals. Unstabilized guncotton, 1, shows an enormous decomposition at the very beginning which quickly slows down. The stabilized guncotton, 2, shows the maximum of changing pressure after the 32nd hour.

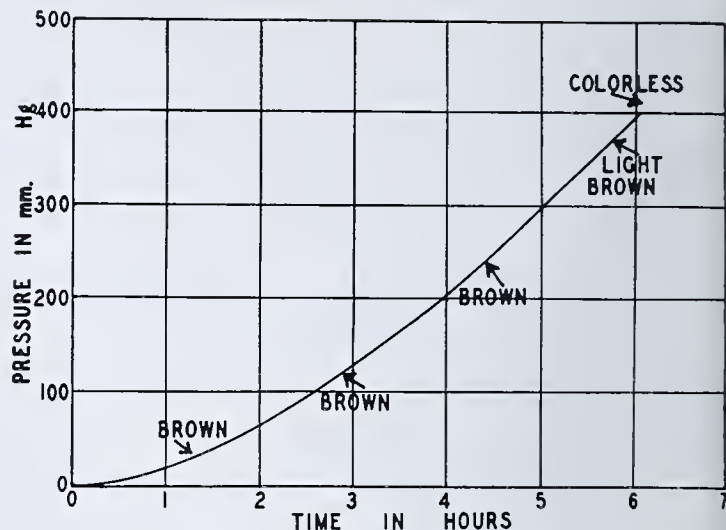


FIGURE 8. COLOR OF DECOMPOSITION GASES

0.0050 gram of stabilized guncotton.  $157^{\circ}\text{C.}$  (uncorrected). Colorless gas becoming brown on admitting air or on standing at  $25^{\circ}\text{C.}$  for 24 hours. Fibrous, orange-brown residue. On standing 24 hours becomes amorphous and dark

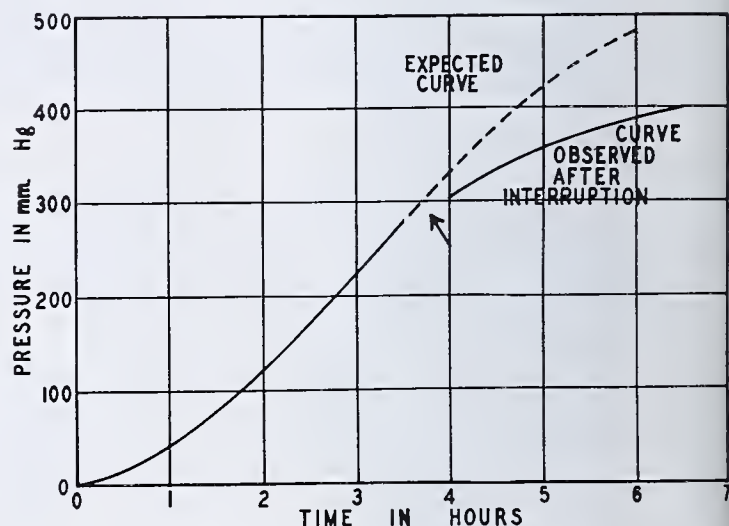


FIGURE 9. EFFECT OF REMOVAL OF DECOMPOSITION GASES

0.0050 gram of stabilized guncotton.  $157^{\circ}\text{C.}$  (uncorrected), in vacuum. Experiment interrupted and gaseous decomposition products removed, heating then continued

Improved methods of stabilization allow the production of completely stable cellulose nitrates without pulping this material. It is known that the pulping process needs time and power. With the right stabilization, one can get exactly the same stability with unpulped as with pulped material, as can be seen from Figure 12. Finally, Figure 13 shows the stabilities which can be obtained with cellulose nitrates made by different methods of nitration. Guncotton was made by nitrating cellulose with a sulfuric acid-nitric acid mixture, with a mixture of nitric acid and phosphoric acid, and with nitric acid and glacial acetic acid. The stabilities of the three different nitrates are practically the same.

## Conclusion

The feather-manometer test which works with 5 or 50 mg. of cellulose nitrate at elevated temperature gives a very interesting and complete insight into the processes which take place if any cellulose nitrate, or other explosive, is heated at temperatures between  $135^{\circ}$  and  $157^{\circ}\text{C.}$ , or higher. These tests can be carried out without endangering the experimenter. They have the great advantage that all decomposition products remain in contact with the cellulose nitrate, so that these may be considered rather severe tests. Cellulose nitrates which are found very stable with the new feather-manometer



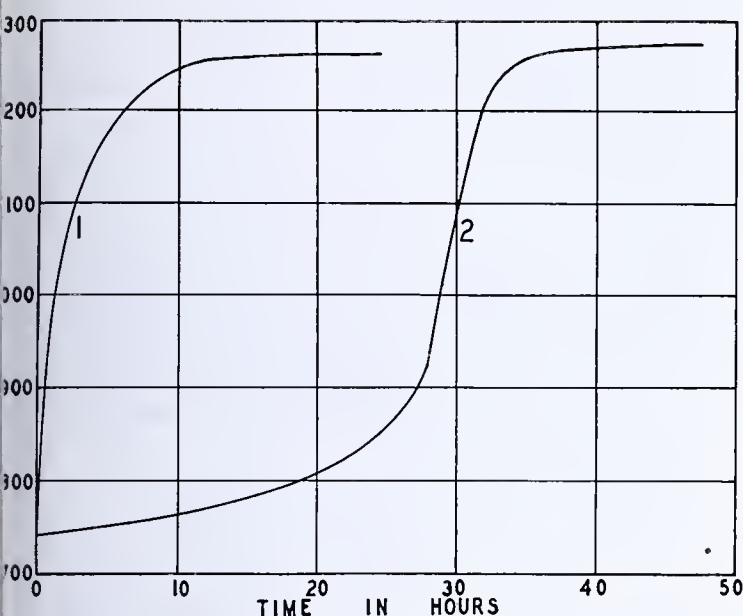


FIGURE 10. DECOMPOSITION CURVES

beginning at atmospheric pressure, 135° C. 532 mm. air pressure at room temperature

1. 0.0050 gram of unstable guncotton
2. 0.0050 gram of same guncotton, stabilized

st are also found very stable with the Bergmann-Junk test, in spite of the fact that this latter test has many weak points.

### Acknowledgment

The authors wish to thank Regis Raab, who assisted with great skill, and E. I. du Pont Nemours & Company, Wilmington, Del., through whose financial help the experiments with the feather manometer have been made possible.

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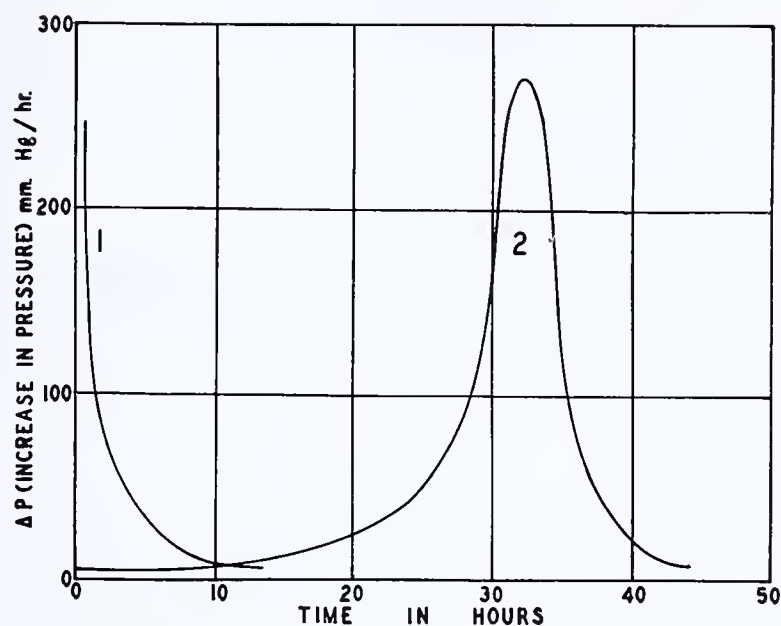


FIGURE 11. PRESSURE CHANGES WITHIN 2 HOURS

1. Unstabilized
2. Stabilized

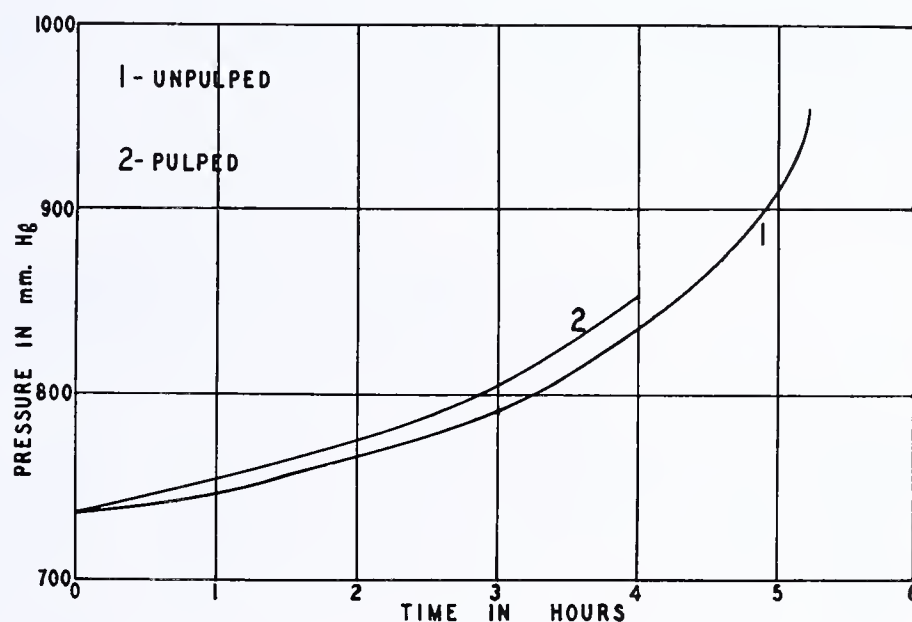


FIGURE 12. EFFECT OF PULPING

0.0500 gram of guncotton nitrated with sulfuric and nitric acids and water. Alcohol-stabilized. 532 mm. air pressure at room temperature. 135° C. (uncorrected)

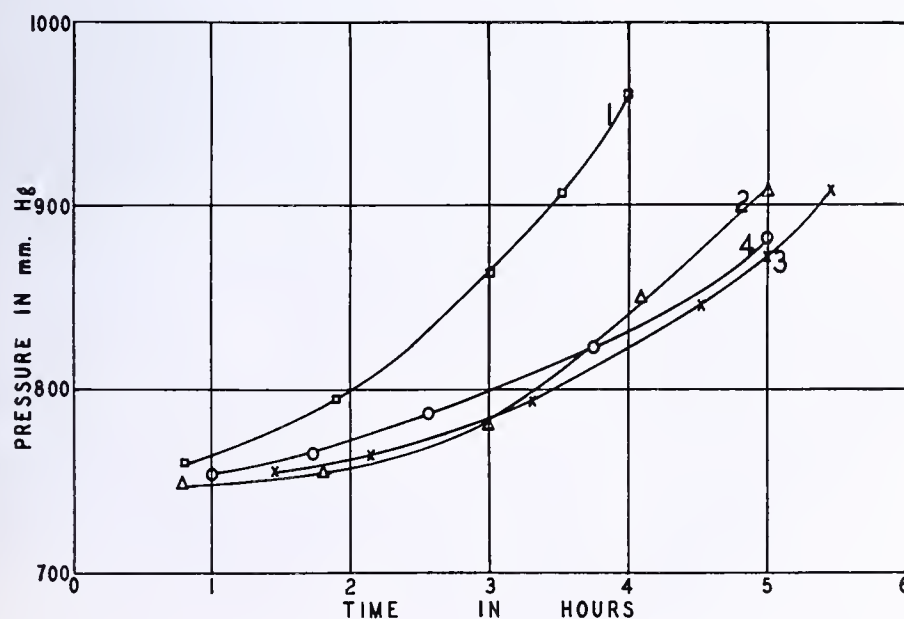


FIGURE 13. STABILITY

0.0500 gram, 532 mm. air pressure at 250° C. 135° C. (uncorrected). Dried 10 minutes at 100° C. at 1 mm. mercury before entrance of air

1. Nitrated with sulfuric and nitric acids and water, stabilized with acid and alkali
2. Nitrated with sulfuric and nitric acids and water, stabilized with alcohol
3. Nitrated with  $H_3PO_4$ ,  $P_2O_5$ , and nitric acid, stabilized with alcohol
4. Nitrated with acetic and nitric acids, stabilized with alcohol



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RECEIVED November 1, 1937. Presented before the Microchemical Section at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C. April 12 to 15, 1937.

## A Procedure for Microfusions

CHARLES VAN BRUNT, General Electric Co., Schenectady, N. Y.

**D**URING a recent investigation of a series of transformation products available only in very minute quantities, using microchemical procedure throughout, insoluble residues of the order of 0.1 mg. in weight were obtained, and it was important to obtain at least a qualitative knowledge of their identity. Scantiness of material required that everything possible be done on a single sample.

In such a situation the analyst naturally turns to a fusion. A search of microchemical literature, however, revealed no record of quantitative analytical fusions with such small amounts. Half-milligram charges could not be handled in even the smallest available platinum crucibles without danger of loss, chiefly because of the tendency of the fused material to creep. Electrically heated platinum ribbon is subject to the same difficulty to a high degree.

Finally a modified bead procedure proved highly satisfactory.

Each residue was obtained in the course of the analysis as a thoroughly washed powder driven into the apex of a microcentrifuge tube. It was withdrawn as a slurry by means of a capillary pipet and deposited upon a platinum ribbon 0.025 × 1.50 mm. which was gently heated by a current. By careful manipulation of the pipet it was easy to concentrate the dried material in about 4 mm. of the ribbon length, all on the upper side. It adhered well enough for the subsequent handling.

The end of a piece of 0.508-mm. (0.020-inch) platinum wire was bent into an elongated crook slightly smaller in external dimensions than the section of ribbon carrying the dry residue. This crook was filled with the desired amount of flux (KNaCO<sub>3</sub>) by the familiar process of dipping and fusion in the microflame. The section of ribbon was then cut out with scissors and received on the corner of a slide. The flux on the wire was next re-fused

and quickly touched to the deposit on the ribbon section held close to the flame on its slide. Ribbon and all were thus picked up. Upon reheating, capillary action at once drew the section into a symmetrical position on the crook and held it there, permitting thorough contact of sample and flux during the subsequent fusion, even with a moderate blast. No tendency to creep was observed. Where creeping occurs, however, it can usually be prevented by using a wide flame with its center directed upon the wire shank beyond the fusion so that the heat gradient is always downward to the fusion.

A decided advantage of this procedure is that the fusion can be dissolved from the wire directly in tubes as small as 2 mm. in bore, thus doing away with the loss or dilution involved in transfer from a crucible.

The procedure is not adapted to pyrosulfate: The excess sulfuric anhydride is lost too rapidly and the direct flame causes reduction. Quartz tubes are best for this. With alkaline carbonate a good fusion may be obtained over the direct microburner flame without important contamination from the sulfur content of the gas.

RECEIVED November 16, 1937.

### Correction

An error was made in printing in our February issue the paper by Foulke and Schneider entitled "The Microtechnic of Organic Qualitative Analysis." In Figure 4, on page 106, tube A and B should have been shown with open, rather than closed ends.



# A Microrefractometer of Simple Design

## Laboratory Construction

A. E. EDWARDS WITH C. E. OTTO, University of Maine, Orono, Maine

A MICROREFRACTOMETER of simple design has been described by Jelley (1). Some details of the construction were not given, but it appears that this experimenter had at his disposal certain apparatus not found in the average chemical laboratory. The present authors have found it possible to construct a similar instrument (Figure 1) using readily available apparatus. They claim originality in the method of preparing the scale and in other minor details of the construction, but not in the principle or design of the apparatus.

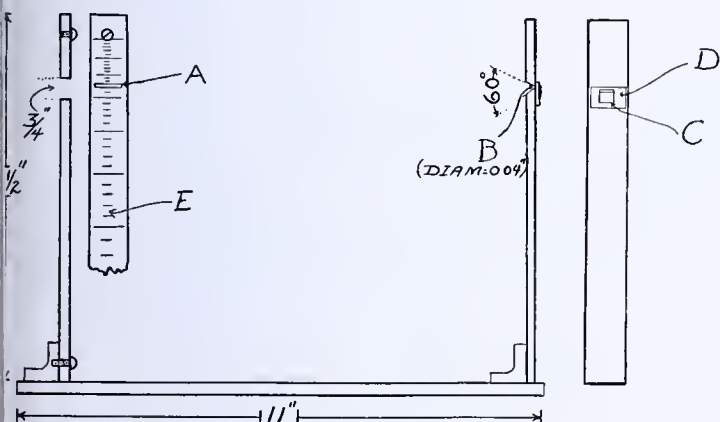


FIGURE 1. DIAGRAM OF APPARATUS

In using this microrefractometer, the slit, *A*, illuminated from behind with monochromatic light, is viewed through a small aperture, *B*. A microscope coverslip, *C*, beveled off on one edge at an angle of approximately  $45^\circ$ , is placed on a microscope slide, so that a small prism is formed (Figure 2) when a drop of liquid is applied to the bevel. The coverslip may be held in place by the capillary attraction of the liquid itself and the slide by binary stage clamps (not shown in Figure 1). The microprism of liquid is adjusted so as partially to cover the aperture, *B*, and since the pupil of the eye is larger than the aperture, the effect is that of a camera lucida in which the virtual image of the slit is seen on the scale, *E*, in a position which indicates the value of the refractive index of the liquid.

The main divisions of the construction of the apparatus were the preparation of the beveled coverslips, construction of the microprism, and determination of the scale divisions. A number of coverslips of the grade commonly used in microscopy were examined for strains under the microscope between crossed Nicols, with the aid of a gypsum plate. Approximately one-third of the coverslips examined were discarded. The edges of the suitable coverslips were cemented together by shellac, and the block of coverslips thus formed was cemented, with one edge projecting, between the two halves of a block of wood, which had been cut in two at an angle of  $45^\circ$ . The projecting edge was then ground by hand by rubbing on a glass plate covered with a suspension of emery powder, and later Tripoli powder, in water and finished in the same manner with jewelers' rouge in water until a smooth glassy surface flush with the lower surface of the wood was obtained. The coverslips were separated by immersion for 24 hours in methyl alcohol, cleaned, and examined under the microscope as before. The best of the coverslips was mounted optically on a slide (using picein cement) and the angle of the bevel was determined by means of a revolving, graduated microscope stage. The coverslip was inverted and the angle of the opposite end of the bevel was determined. The two values agreed within  $25'$ .

The frame was made from  $5 \times 0.63$  cm. ( $2 \times 0.25$  inch) flat bar stock, and was coated with varnish to prevent corrosion. Dimensions and other details can be obtained from Figure 1.

To determine the scale graduations, the optical system at the microprism, as shown in Figure 2, had to be considered.

If the angle of the bevel is  $\alpha$ , the refractive indices of the coverslip and of the liquid,  $N_c$  and  $N_l$ , respectively, and the angle of deviation,  $\gamma$ , by the law of refraction

$$\sin \beta = \frac{N_l}{N_c} \sin \alpha \quad (1)$$

and 
$$\sin \gamma = N_c \sin (\beta - \alpha) \quad (2)$$

The angle  $\beta$  can be understood better by referring to Figure 2 than by a verbal definition.

The refractive index of the coverslip was easily determined by putting the instrument into operation with a blank sheet of cardboard in place of the scale. Various liquids with widely separated indices of refraction were obtained. A Pulfrich refractometer (this might have been replaced by any other reliable refractometer) and the microrefractometer were set up side by side. The refractive index, as determined by the Pulfrich refractometer, and the position of the virtual image of the slit on the scale of the microrefractometer were obtained simultaneously for four liquids. This procedure dispensed with temperature considerations. The distance from the slit to the position of each image was measured by a micrometer caliper, and this divided by the distance to the microprism behind aperture *B* gave the tangent of  $\gamma$ . Combining Equations 1 and 2 by eliminating functions of  $\beta$  and solving for  $N_c$  gave

$$N_c^2 = \frac{\sin^2 \gamma}{\sin^2 \alpha} - 2N_l \frac{\sin \gamma}{\tan \alpha} + N_l^2$$

Substitution of the data obtained into this equation yielded four values of the refractive index of the coverslip. The average of the four values of  $N_c$  was obtained. Maximum deviation of individual values from the mean was slightly over 0.1 per cent. The coverslip was cut, normal to the beveled edge, into three pieces, by scratching lightly with a diamond chip and breaking along the scratches by light pressure. This was done to lessen the loss in case of accidental breakage, and to allow the usage of smaller volumes of liquids.

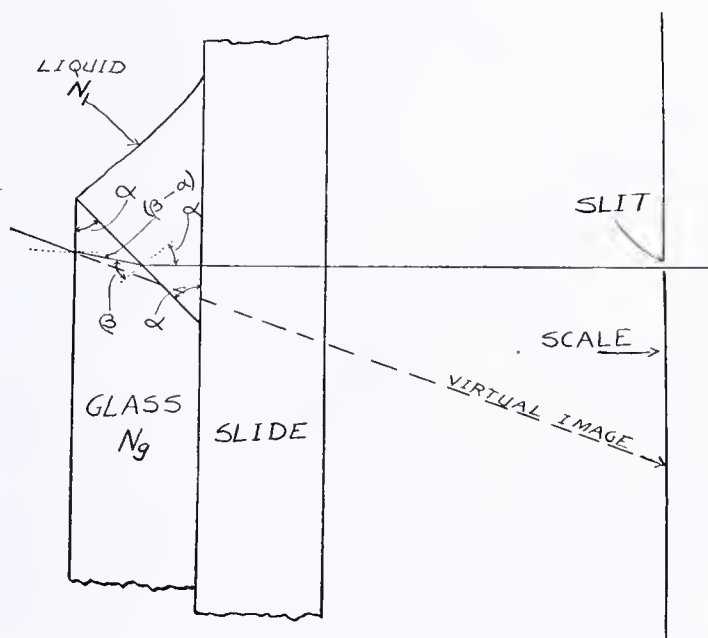


FIGURE 2



Practice on other coverslips before attempting to use this method on the beveled slip is advised. The refractive index of the glass being known, the scale for the three beveled slips was calculated by substituting in Equations 1 and 2, a separate calculation of scale distance being made for each 0.01 increment in the value of  $N_i$  from 1.330 to 1.850.

TABLE I

Liquid	Refractive Index		Deviation %
	Microrefractometer	Pulfrich refractometer	
Water	1.332	1.33279	0.1—
Amyl alcohol	1.398	1.40123	0.2+
Benzene	1.491	1.49297	0.1+
Pyridine	1.504	1.50651	0.2—
Aniline	1.576	1.57854	0.2—

The instrument when completed was found to require volumes of liquids of the order of 0.01 ml. It gave values of the refractive index agreeing with those obtained by the use

of a Pulfrich refractometer to within 0.3 per cent. This is illustrated by the data in Table I obtained by setting up the two instruments side by side and making corresponding determinations practically simultaneously.

Variations of room temperature within a few degrees do not cause deviation of the values obtained beyond the limit of experimental error given above. However, if values at exact or elevated temperatures are required, they can easily be obtained, as suggested by Jelley (*1*), by fitting a hollow circular disk into the frame behind the microscope slide and circulating water of the desired temperature through this disk.

The total cost of the instrument was \$1.00 for material and \$3.00 for the services of a mechanic.

### Literature Cited

- (1) Jelley, E. E., *J. Roy. Microscop. Soc.*, 54, 234-45 (1934).

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## Microdetermination of Arsenic

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**A modified Gutzeit procedure capable of determining as little as 0.1 microgram of arsenic with a probable error of 5 per cent and sensitive to 0.01 microgram of arsenic is described.**

A PROPOSED investigation of conditions conducive to the entrance of arsenic into the eyes of individuals undergoing treatment with organic arsenicals necessitated an analytical procedure capable of determining 0.1 microgram of arsenic with less than a 5 per cent error.

A search of the literature revealed seven micromethods for arsenic. Of these, the Bettendorf (*19, 39, 62*) test was discarded almost immediately; for, although it is sensitive, little or no successful work has been done toward its application as a quantitative measure. Three others, the Denigès (*4, 21, 48, 61*), Reinsch (*23, 56*), and titration (*1, 5, 9, 16, 24, 43, 49, 51, 63*) methods seemed to lack the requisite sensitivity; although one variation, the sensitive and accurate conductometric titration of Jander and Harms (*37*), possesses the single disadvantage of requiring the separation of arsenic from the digestion residues. The Marsh-Berzelius method (*27, 31, 46, 47, 52, 60*), although very sensitive, is cumbersome and in common with the original Gutzeit spots possesses the disadvantage that quantities intermediate to those used in the standard determinations cannot be determined with a measurable degree of accuracy. The most accurate use of the nephelometer (*3, 41, 42*) involves a fairly elaborate setup, and the procedure is long and does not appear to be as sensitive as the Marsh or Gutzeit methods. The electro-Gutzeit method (*25, 45, 57*) has been used very successfully, but in preliminary experiments at this laboratory the zinc-acid process was somewhat more sensitive.

Flückiger (*26*) used the zinc-acid Gutzeit procedure as long as 48 years ago to detect 0.1 microgram of  $As_2O_3$ , though he placed the workable limit of the process at  $1\gamma$ . Since then at least four authors (*12, 38, 50, 58*) have differentiated between  $0.1\gamma$  and  $0.2\gamma$  by means of this procedure. Heretofore, the advantage of this sensitivity was offset by the relative inaccuracy of the method. Where figures are available, the approximate average error in the lower concentration ranges of the nephelometric, Denigès, and titration procedures (with the exception of the very accurate titrations of Gangl and Sanchez, *28*) is about 5 per cent, that of the Gutzeit method about 8 per cent. The author could find only two papers in which the accuracy of this

process was studied. In one of these (*6*) the probable error ranged from 50 to 8 per cent; in the other (*55*) it was uniform at 10 per cent for single determinations. These errors have been greatly reduced by using the apparatus and procedure developed in this laboratory following a study of the various conditions controlling the reaction.

### Experimental

Nearly all authors used paper disks or strips in the Gutzeit procedure. The former not only possess the disadvantage of inaccuracy, but also, as shown by the work of Cribb (*17*), allow a measurable portion of the arsine to pass through apparently unchanged. The paper strips, prepared in any of the usual ways, must necessarily possess some unevenness of deposition due to unpreventable drainage. Also it seems difficult to avoid errors up to 5 per cent in width when cutting the smallest size (1 mm.) strips.

As a first effort to avoid these difficulties, the usual tube and paper strip were replaced by a capillary tube with a thin film of mercuric chloride deposited by evaporation of an alcoholic solution on the inner wall. When using these tubes it was necessary to pass the gases from the generator over a drying agent such as calcium chloride, or through a micro condenser, since condensed moisture inside the mercuric chloride tube would streak or wash away the deposit. A series of such tubes, matched for depth and uniformity of deposit, gave very consistent results when exposed to arsine and "developed" by hydrogen iodide. However, the difficulty of reproducing a standard deposit was so great that the method was considered impractical. Deposits from solutions of mercuric chloride in acetone, in ether, and in water were not as good as those obtained from the alcoholic solution. Results from the use of mercuric bromide and silver nitrate



solutions were decidedly inferior to those obtained from mercuric chloride deposits. A lesser hindrance to the use of these tubes was the indefinite termination of the stain. This is also observed on paper strips, and may be due to the large volume-surface ratio.

This ratio may be reduced to a minimum by substituting cotton for paper as practiced by Hünnerbein (35), but much better results are attained by having the mercuric chloride deposited on a string which fits fairly tightly in a capillary tube. The termination of the stain is then consistently definite, but a string which hangs freely or not quite snugly stains with an indefinite end point. This may have been a cause of Thompson's (59) lack of success with thread as reported by Sanger and Black (58), although Cahill (13) used No. 60 thread impregnated with mercuric bromide to determine arsenic down to  $0.5\gamma$  with 10 to 15 per cent error.

During the work on mercuric chloride-coated tubes, it was observed that an apparent sublimation of the finely divided deposit occurred at temperatures as low as  $80^{\circ}\text{C}$ . This suggested that the mercuric chloride might be distributed very evenly over impregnated and cut strings by heating them in sealed tubes. Experiments at various temperatures and periods in evacuated and nonevacuated glass tubes sealed at both ends indicated that a temperature of  $100^{\circ}\text{C}$ . for one hour in a nonevacuated tube was most successful. It was necessary to pack the strings tightly in the tube, and advantageous to keep the tube revolving during the heating process. When small quantities (less than twelve) of strings were so treated, there was a noticeable increase in uniformity of results. This was not observed, however, when large quantities were heated; and since it was necessary to have at least 100 uniform strings for a series of experiments, the heat treatment was discarded. An effect similar to that obtained by heating a small quantity of strings was secured by closely packing about 150 strings in a tightly stoppered tube and storing in darkness at room temperature for 1 to 2 weeks. The stains were then more uniform and somewhat longer.

Strings impregnated from alcoholic solutions were superior to those soaked in aqueous, ethereal, or acetone solutions. Mercuric chloride proved much more satisfactory than the mercuric bromide which has become so popular with the users of paper strips. Strings were prepared from a number of alcoholic solutions of different concentrations. The most satisfactory solution strengths were found to differ considerably from those in previous use. The lowest concentration (0.25 per cent) that gave a discernible stain was selected for use where less than  $4\gamma$  of arsenic would be involved. String soaked in a 5 per cent solution was used where 4 to  $100\gamma$  of arsenic were to be determined.

A number of substances were tried as developers. The iodides of lithium, potassium, and cadmium all developed light brownish to yellow color, with considerable variation of intensity, and subsequent rapid fading. Two easily produced compounds which have not previously been applied to this use

gave much more intense, definite, and permanent development. One of them, osmic acid, is too expensive and noxious to be satisfactory, although the developed color was as good as that produced through the use of ammoniacal silver nitrate, the reagent finally selected as most satisfactory for this procedure. The silver stain does not fade; several hours' exposure to daylight darkens the whole string, but this can be avoided by washing the string in dilute ammonium hydroxide solution and rinsing in distilled water. However, it is not necessary to preserve the stain, since the averages of the measured lengths of the standard stains are graphed and the measurements of stains produced by unknown quantities of arsenic are applied to this curve. The earliest use of the graph that the author could find was Collins' (15) adoption of it in 1918. It has since played an indispensable part in the procedures of at least five other workers (6, 30, 36, 40, 55).

The physical treatment of the string during the reaction was found to be more important than the subsequent color development. Changes in the length and character of the stain accompanying marked variations of room temperature led Heidenhain (34), Crossley (18), and the author to control the temperature of the absorption tube. Heidenhain immersed the whole apparatus in a water bath at  $30^{\circ}\text{C}$ . Crossley made a condenser inner tube of the absorption tube and passed tap water through the jacket, with the reaction flask submerged in a  $20^{\circ}$  water bath. The author employed two water baths; one to control the temperature of the reaction

vessel and scrubber tubes, the other to control the temperature of the absorption tube, as shown in Figure 1. With this apparatus it was possible to study the relationship between temperature and character of stain in some detail. Twenty-two temperature combinations were tried, ranging from  $40^{\circ}\text{:}50^{\circ}\text{C}$ . to  $15^{\circ}\text{:}10^{\circ}\text{C}$ . for reaction and absorption, respectively. The optimum range for the reaction and for the absorption temperature was from  $15^{\circ}$  to  $30^{\circ}\text{C}$ . However, the number of working combinations is limited by the fact that best stains are obtained when the absorption temperature is about  $5^{\circ}$  lower than the reaction temperature. When this condition is observed, the length and character of the stains vary almost imperceptibly from  $20^{\circ}\text{:}15^{\circ}\text{C}$ . to  $30^{\circ}\text{:}25^{\circ}\text{C}$ . The author is using the latter combination because it is more suitable for all-year use in St. Louis. Exact temperature control is not very important, and a variation of  $1^{\circ}$  or even  $2^{\circ}$  makes no perceptible difference in the stain; but the end point becomes rather indefinite when the two temperatures are equal, and almost impossible to determine with any accuracy when the absorption temperature is much higher than the reaction temperature. The success of the temperature ratio set forth here might be ascribed to condensation of water vapor.

The desirability of a high, uniform moisture content for the gases has been frequently mentioned (18, 22, 24, 29, 33, 44, 50, 53, 58). The usual method of ensuring an adequate concentration of water vapor has been to pass the gases through a cotton plug saturated with

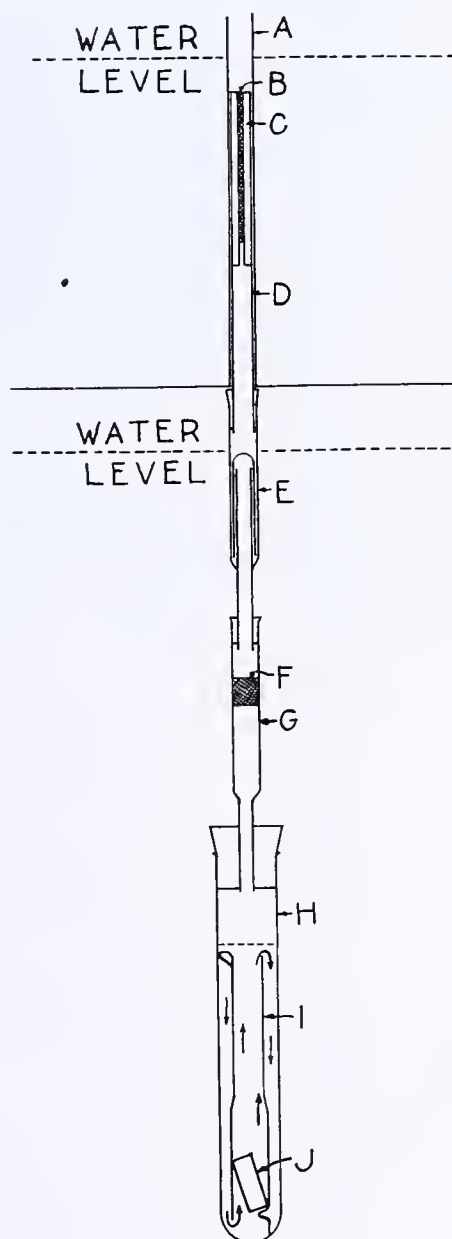


FIGURE 1



water. For this purpose, however, the water trap described under Apparatus has proved definitely superior to the cotton or gauze plug.

Lead acetate is a very satisfactory medium for removal of hydrogen sulfide from the generator gases. von Fellenberg's (24) use of bandage material suggested the gauze plug which is used in the lower scrubber tube.

The 50-ml. Erlenmeyer flasks first used as reaction vessels were discarded in favor of the more efficient form illustrated in Figure 1. The position of the metal in the inner tube makes it certain that the rising gases will set up a circulation of the fluid as indicated by the arrows. This flow serves two purposes: The fluid is effectively cooled to the temperature of the water bath, assuring the maintenance of a constant temperature; and all the solution is constantly passing over the active surface of the metal at a uniform rate, ensuring an even diminution of arsenic content and evolution of arsine.



FIGURE 2

The size of the reaction vessels and digestion flasks determined the concentration of sulfuric acid in the reaction fluid at about 3.5 *N*.

At this concentration, ordinary c. p. zinc dissolves rapidly, but there is a fairly long lag before the reaction becomes visually perceptible. To avoid this period, various methods of sensitizing the zinc have been used (2, 14, 18, 22, 44, 46, 47, 53, 55). Immersion in 0.5 per cent copper sulfate solution, in 1 to 3 hydrochloric acid containing 0.5 per cent of stannous chloride, and in 1 to 3 hydrochloric acid was tried in this laboratory. The last was most successful. Exact control of the length of time the zinc is allowed to react with the acid is not important, as the same results were obtained from pieces of zinc which had been in the acid for 5-, 10-, and 15-minute periods. It was found unnecessary to keep the sensitized sticks under water. Those washed and dried by spontaneous evaporation and handled by galvanized forceps were just as good or better at any period after preparation than pieces which had been kept under water. A zinc-copper couple would eliminate the necessity for this preliminary treatment, but results obtained were not as satisfactory.

Very little arsine is evolved in the absence of stannous and ferrous ions (2, 32). A series of experiments showed that wide variation in the amount of stannous ions was allowable, but that more than 10 drops of a 40 per cent solution of stannous chloride in concentrated hydrochloric acid were undesirable. The amount adopted was 5 drops to 40 ml. of 3.5 *N* sulfuric acid. Similarly it was demonstrated that the best concentration of ferrous ions lay between 0.05 and 0.20 gram of Mohr's salt in each 40 ml. of the acid. One-tenth gram was chosen as the standard.

L. T. Throne, in the discussion of a paper by Goode and Perkin (29), stated that he found an alloy of zinc with 2 per cent cadmium to be very sensitive and reliable. The author tried alloys of 0.5 and 2 per cent cadmium, 0.1 to 10 per cent tin, 0.5 to 5 per cent lead, and 0.5 per cent magnesium. When these metal mixtures were used, the addition of stannous or ferrous salts to the reaction fluid was unnecessary. An alloy of 0.5 per cent tin was

adopted for subsequent work. The stains obtained were as consistent as before but longer, and the procedure was simplified.

One lot of very pure zinc reacted very slowly with sulfuric acid. The tin alloy made from this zinc required 2 hours to develop a stain previously obtained in 30 minutes. The time could be shortened by using higher concentrations of acid, but the stains were not as uniform. The addition of 0.1 gram of Mohr's salt to the reaction mixture when this alloy was used helped the reaction to "completion" in 45 minutes. The weighing of Mohr's salt for each experiment was rather time-consuming, and an effort was made to eliminate the need for this salt.

To this end artificial impurities in the form of platinum, lead, nickel, and iron were added to separate portions of the zinc-tin alloy in various amounts, each less than 1 per cent. Platinum was satisfactory in a concentration of 0.01 per cent. The lead alloy gave a very intense and definite coloration, but the reaction was still slow and the stain not very long. On the other hand, the reaction with 0.1 per cent nickel was so vigorous that the strings were blown out of the tubes.

Iron produced about the same result as nickel, and was used in diminishing concentrations for subsequent preparations. In the range of 0.001 to 0.005 per cent a rather remarkable variation in the rate of reaction was noted. Sticks of alloy containing 0.001, 0.002, 0.003, 0.004, and 0.005 per cent of added iron all originally of the same size could, after reacting with 40 ml. of 3.5 *N* sulfuric acid at 30°C. for 45 minutes, be visually separated and arranged in order according to the iron content (Figure 2). In sticks originally weighing 6.5 grams, there was on the average a loss of 0.75 gram for each 0.001 per cent of iron over the first 0.001 per cent. The weight lost and the amount of arsine produced by the alloy with 0.001 per cent of added iron varied little from the effect secured by the pure zinc-tin alloy. This was also true of samples containing 0.001 per cent of nickel, and 0.001 per cent of platinum. On the basis of the appearance of stains obtained through the use of these alloys, the best concentration of iron seemed to lie between 0.002 and 0.003 per cent. An alloy with 0.0028 per cent of iron was compared with one containing 0.01 per cent of platinum. The former was more consistent and was selected for further work, although the stains obtained from its use were somewhat indefinite. It had been noticed earlier that lead appeared to have a stabilizing influence on the reaction between the metal and acid. With this in mind, 0.01 per cent of lead was added to the selected iron alloy. The stains obtained were very dark and definite, with no loss of reproducibility.

A second lot of very pure zinc was found to have a slightly greater iron content than the first. A comparison of percentage of iron-weight lost curves of alloys made of zinc from the two lots (Figure 3) indicates that lot II contained approximately 0.0008 per cent more iron than lot I. In conformity with conclusions drawn from the work on lot I, the addition of 0.0020 per cent of iron to lot II was most satisfac-

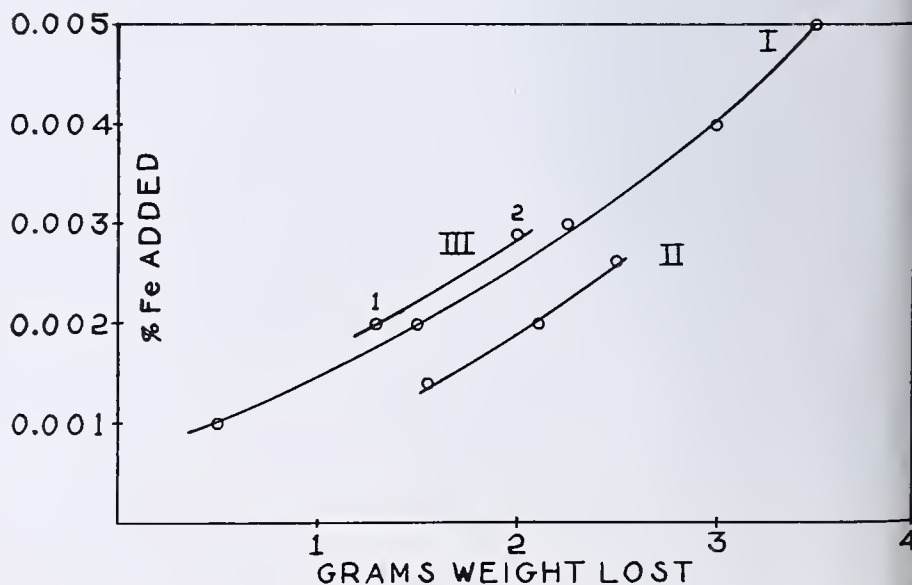


FIGURE 3



tory. In general, it seems that the best results are obtained when the iron content is such that under the given conditions of dissolution the weight loss of approximately 6.5-gram pieces lies between 2.0 and 2.5 grams.

Use of this generalization is illustrated in Figure 3. A small sample of a third lot of pure zinc was used to form an alloy containing 0.0020 per cent of added iron. Several sticks of this alloy were allowed to react with acid under the standard conditions noted above. The average loss of weight was plotted against the percentage of added iron as point 1.

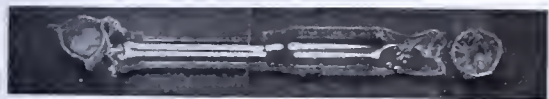


FIGURE 4

A line having the same curvature and slope as lines I and II was then drawn through this point. On the basis of this graph it was predicted that an average weight loss of 2.1 grams could be secured by the addition of 0.0029 per cent of iron to alloy made with the zinc of lot III. How well this prophecy was fulfilled is demonstrated by point 2, which shows the average loss of weight of several sticks of lot III alloy to which 0.0029 per cent of iron had been added. This use of the graph and the generalization made above shortens the time and labor required to determine the percentage of iron needed by any particular lot of this pure zinc.

Although the effect of small variations in the iron content of the alloy is pronounced, the quantity of iron in the acid solution seems to be relatively unimportant. One-tenth gram of Mohr's salt added to each tube of a series made no difference in the length of stain.

It was found that a difference in casting temperature of as much as 100° C. caused a slight but definite difference in the length of the stain produced through the use of the alloy. Heretofore reference to this effect has been neglected by workers in this field, although Bolley (11) long ago recorded a more marked effect of extreme casting temperatures on the acid dissolution of pure zinc. Because of this variation, castings are made in this laboratory when the metal is at a temperature of 480° to 500° C.

It is probably needless to add a word of caution concerning the danger of contaminating the alloy. The porcelain or quartz vessels used as melting pots should be thoroughly cleaned by boiling in the digestion mixture of acids. The mold and vessels should be seasoned and tested by casting several preliminary small quantities before a large amount of alloy is made.

The digestion procedure was selected by comparing results obtained from digestions of blood samples containing known amounts of neoarsphenamine. On the basis of rapidity or completeness of reaction, or both, the mixture of perchloric, nitric, and sulfuric acids described under Reagents was superior to nitric-sulfuric, perchloric-sulfuric, perchloric-nitric, hydrogen peroxide-sulfuric, and fuming nitric-sulfuric mixtures and combinations.

The process can proceed more rapidly when some device is used to prevent bumping. Glass beads proved slightly better for this purpose than crushed glass fused to the bottom of the flask.

Prolonged boiling of the sulfuric acid solution after elimination of the last traces of perchloric acid is unnecessary. Two or three minutes of boiling following the disappearance of the intense yellow coloration is sufficient.

Residual traces of nitrogen need not be removed from the digestion fluid when the determination is made as described. The use of oxalic acid made no detectable difference in the

character or length of the stains obtained through the use of any of the digestion mixtures mentioned.

Barnes and Murray (6) found, contrary to the usual belief, that charring during digestion does not affect the final result. The author's experience, at present limited to recovery of known amounts of arsenic from 1-ml. samples of blood, is in accord with their finding. Determinations were quantitative regardless of the amount of carbon formed.

The author also concurs with Klein (40) in finding that the effect of the presence of moderate amounts of chloride in the digestion is negligible.

Following digestion, the pentavalent arsenic is reduced to the trivalent state in order to increase the length of stain and uniformity of results, using the method of Davis and Maltby (20) with very slight modifications. Three series of quantities of 0.02, 0.075, 0.1, and 0.2 gram of sodium bisulfite were tried in this procedure. One-tenth gram was chosen as the standard quantity for future work since the differences, though slight, were consistent. Potassium metabisulfite was as satisfactory as sodium bisulfite in this reduction procedure. Hydrazine sulfate and potassium iodide gave low results. The use of bisulfite, hydrazine, or Mohr's salt as a reducing agent in the concentrated digest was very unsatisfactory.

Since the arsenic in arsenic trioxide and neoarsphenamine added to "normal" (containing less than 0.01% of arsenic per milliliter) blood was fully recovered, the lengthy process of dry ashing (fusion) was not tried.

Determinations were made on arsenic which had been isolated from the products of digestion by distillation as the trichloride (5, 7, 8, 21, 42, 63) and by adsorption on ferric hydroxide (46, 47, 54). No increase in amount or uniformity of recovery could be obtained.

### Apparatus

The generator consists of a 23 × 150 mm. Pyrex test tube, *H*, with an inner tube, *I*, as shown in Figures 1 and 4. The height of this inner tube should be so adjusted that when the tube containing a piece of zinc 20 mm. long and 8 mm. in diameter is placed in the generator tube the lowest point of the meniscus of 40 ml. of water will be 4.0 to 4.5 mm. above the top of the inner tube.

The gases are passed through two 10 × 65 mm. wash tubes, the first containing a plug of cheesecloth (Figure 1, *F*), made by rolling a 9 × 90 mm. quadruple thickness strip of the material; the second is a glass trap. Both tubes *G* and *E* are illustrated in Figure 1. The absorption unit is completed by the string tube, which consists of a capillary tube of 1.3-mm. bore, 7.5 mm. in outside diameter, and 60 mm. long (Figure 1, *C*), welded to a tube of the same length and outside diameter, but of 4.3-mm. bore (Figure 1, *D*). It is essential to avoid constriction of the capillary tube at the weld.

The generator and wash tubes are immersed in a water bath maintained at 30° C. The string tube projects into a closely fitting copper tube (Figure 1, *A*) which is surrounded by water at 25° C.

When less than 4% of arsenic is to be expected, a quartz 23 × 150 mm. test tube is used as the digestion flask. When the amount of arsenic is likely to exceed 4%, a Pyrex micro-Kjeldahl flask of about 12-ml. capacity, of the newer "arsenic-free" glass, is used.

Two Pyrex glass beads 5 mm. in diameter are placed in each digestion flask to prevent bumping. Beads are unnecessary when opaque quartz tubes are used.

A piece of opal glass or other white background should be provided as an aid to the measurement of the black stain.

An excellent mold for casting the alloy sticks can be made by clamping two carbon plates (welding plates) 15 mm. thick face to face and drilling 8-mm. holes at 25 mm. intervals along the junction as a midline.

Several porcelain (or quartz) casseroles or evaporating dishes of 50- and 200-ml. capacities should be cleaned and seasoned.

### Reagents

Concentrated sulfuric acid.

The digestion mixture consists of 60 per cent perchloric, concentrated nitric, and concentrated sulfuric acids in the proportion 1 to 1 to 4.



Sodium bisulfite in 0.1-gram amounts.

Lead acetate solution, 2 *N*, acidified with acetic acid.

Hydrochloric acid, 1 to 3.

Alloy consisting of zinc, tin, lead, and iron in the following proportion by weight: 99.5 to 0.5 to 0.01 to about 0.0028. The exact proportion of iron must be determined by actual trial in the laboratory. The alloy is cast into sticks 8 mm. in diameter and cut into 20-mm. lengths. These are immersed in 1 to 3 hydrochloric acid for 5 minutes, washed with distilled water, allowed to dry on a clean glass plate, and stored in a glass-stoppered bottle. These sensitized pieces of alloy should be handled only by galvanized forceps.

Silver nitrate, 2 per cent in ordinary dilute (1 to 10) ammonium hydroxide.

The string used was Morse and Kaley No. 8 knitting cotton. Some care must be exercised to secure even deposition of the mercuric chloride. The most successful procedure used in this laboratory is as follows:

The string is wound as loosely as possible in spiral form on a glass tube 5 cm. in diameter and about 35 cm. long, with a space of 1 to 2 mm. between adjacent turns, and is placed in a glass cylinder about 6.5 cm. in diameter and 45 cm. long. The inner tube is held in place by removable glass spacers at each end of the tube, which keep the string from touching the wall of the cylinder. The cylinder is filled to a height of about 5 cm. above the top of the inner tube with a 5 or 0.25 per cent alcoholic solution of mercuric chloride, stoppered, and allowed to stand 15 to 20 hours. The excess solution is then pressed from the string by passing it through a wringer made of seamless rubber tubing on glass rod and driven at moderate uniform speed by a small laboratory motor. The string is fed through the wringer directly from the tube, which is not removed from the cylinder full of solution. After passing through the wringer, the string should be spiraled lightly on a solid drum across the room or, still better, at the far end of a draftless hallway. If the building is equipped with an elevator, excellent results may be obtained by allowing the wrung string to hang down the closed shaft until dry. Avoid drafts! When the string is completely dry it is cut in 18- to 20-cm. lengths and stored in a 23 × 250 mm. tightly stoppered glass tube which has been covered by black paper. In these operations the string should be exposed to daylight as little as possible.

The stock solution of arsenic for standardization is made as described by Lachele (44). About 25 ml. of 20 per cent sodium hydroxide are used to dissolve 1.3208 grams of arsenic trioxide. This solution is saturated with carbon dioxide and diluted to 1 liter with recently boiled distilled water.

A 5-ml. portion of this stock solution is diluted to 15 ml. in a 50-ml. Erlenmeyer flask and acidified with one drop of concentrated sulfuric acid. One-half gram of sodium bisulfite is then added and the flask is heated in a water bath to 80° to 85° C. for 30 minutes. It is then boiled for 2 or 3 minutes or until no trace of sulfur dioxide can be detected in the vapor. The reduced solution is then diluted to 500 ml., a concentration of 10γ arsenic per ml. More dilute solutions are made from this the day they are used.

## Procedure

1. Add 6 ml. of the digestion mixture to the sample in a micro-Kjeldahl flask containing two 5-mm. Pyrex glass beads,

or in an opaque quartz tube, and boil until fumes of sulfur trioxide appear. Continue boiling about 5 minutes. Cool.

2. Transfer the digested mixture to a 50-ml. Erlenmeyer flask and rinse the Kjeldahl flask with three or four small portions of distilled water, making the volume up to about 15 ml. Cool and add 0.1 gram of sodium bisulfite. Cover the flask with a glass bulb and heat for 30 minutes in a water bath maintained at 80° to 85° C. Then boil the contents of the flask for 2 or 3 minutes or until no trace of sulfur dioxide can be detected in the vapor.

3. Transfer contents of flask to a generator tube, increasing the volume to 40 ml. If steps 1 and 2 can be omitted, dilute the sample to 36 ml., and acidify with 4 ml. of concentrated sulfuric acid. Place the tube in the 30° water bath for 15 to 20 minutes.

4. To prepare the absorption unit, place 5 drops of distilled water in the trap, moisten the gauze plug in the other tube with 5 drops of the lead acetate solution, and connect the two as shown in Figure 1. Connect the capillary end of the string tube to a vacuum line, draw in the string, and disconnect the tube from the line, leaving about 1 cm. projecting at the capillary end and 3 to 4 cm. at the lower end. Cut off about 2 cm. of this lower end (handle only this lower end when inserting string in tube), and draw the string up into the tube until the freshly cut end is 1 cm. above the weld. Cut off the projecting length of string, insert the lower end of the tube into a stopper, and connect to the trap to complete the absorption unit.

5. Remove the generator tube from the water bath, insert the inner tube which already contains the piece of alloy (Figure 1, *J*), and immediately stopper with the absorption unit. Submerge the generator and lower scrubber tube in the 30° C. water bath, with the absorption tube in the copper jacket maintained at 25° C. After 45 minutes remove from the water bath and disconnect generator and absorption unit.

6. Remove string from absorption tube and immerse for a moment in silver nitrate solution. Then place the developed string on a spot plate or piece of opal glass and use a vernier caliper to measure the length of the stain.

## Discussion

Each step in the foregoing procedure, each reagent, and each piece of apparatus was adopted only after comparison with existing methods and various modifications of these methods. Since selection was made on the basis of reproducibility, the modifications of method were compared by series of three to ten (usually five) determinations.

The absorption tube shown in Figure 1, *C, D*, gives definitely more uniform results than a single length of capillary tubing. This construction was suggested by the thought that the gases would pass more slowly through the wide portion, and would therefore be more uniformly cooled than when forced through the capillary with greater velocity.

The position of the lower end of the string at 1 cm. above the weld in the absorption tube was almost arbitrarily chosen after a great number of determinations had been made with strings at various heights.

Strings which were first cut in the required lengths and then soaked in solutions of mercuric chloride were not nearly so satisfactory as string prepared as described above.

The exact strength of the silver nitrate solution is not important, but a greater concentration than that specified is unnecessary—even undesirable above 10 per cent. However, the color is not as black if the solution contains less than 0.5 to 1 per cent of silver nitrate.

It was found that a water-trap scrubber tube of the dimensions given should not contain more than 5 drops of water because of the danger of wetting the string. The number of drops should never be varied, because the character of the stain is so intimately related to the moisture content of the

TABLE I. MICRODETERMINATION OF ARSENIC

As $\gamma$	Length of Stain										Av. Cm.	P. E. of Single De-termination	
	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.		%	%
	String 21, from 0.25 Per Cent HgCl <sub>2</sub>												
0.1	0.26	0.25	0.26	0.28	0.27	..	..	..	..	..	0.26	1.4	3.2
0.3	0.60	0.56	0.54	0.55	0.54	..	..	..	..	..	0.56	1.3	3.0
0.5	0.81	0.85	0.81	0.88	0.83	..	..	..	..	..	0.82	1.2	2.8
0.7	1.22	1.11	1.08	1.15	1.21	..	..	..	..	..	1.15	1.6	3.6
1.0	1.51	1.63	1.51	1.63	1.58	..	..	..	..	..	1.57	1.1	2.5
1.5	2.01	2.10	2.06	2.10	2.00	..	..	..	..	..	2.05	0.67	1.6
2.0	2.77	2.71	..	..	..	..	..	..	..	..	2.74	..	..
String 19, from 5 Per Cent HgCl <sub>2</sub>													
5	0.43	0.42	0.40	0.44	0.44	..	..	..	..	..	0.43	1.2	2.6
10	0.56	0.60	0.61	0.61	0.66	0.61	0.66	0.62	0.62	0.66	0.62	1.1	3.5
20	1.08	0.94	1.05	1.09	1.05	1.02	1.02	1.06	1.06	1.00	1.04	0.90	2.8
40	1.79	1.72	1.78	1.95	1.68	1.86	1.82	1.79	1.81	1.78	1.80	0.83	2.7
60	2.60	2.65	2.70	2.64	2.51	2.39	2.44	2.70	2.49	2.54	2.57	0.89	2.8
80	3.09	3.68	3.41	3.24	3.27	3.05	3.15	3.06	3.13	..	3.23	1.4	4.3
100	3.87	3.87	3.89	3.98	3.91	..	..	..	..	..	3.90	0.35	0.77



gases. This last consideration also applies to the amount of lead acetate solution used in the lower tube. Blood digestions clear very rapidly and after water and nitrogen oxides have been driven off the solution assumes a deep canary-yellow color. The temperature rises, and dense white perchloric fumes appear. When the perchloric acid has been eliminated the liquid retains only an extremely faint straw coloration. This color change is sharp; and the boiling need be continued only 2 or 3 minutes after it occurs. The fluid becomes water-clear on cooling.

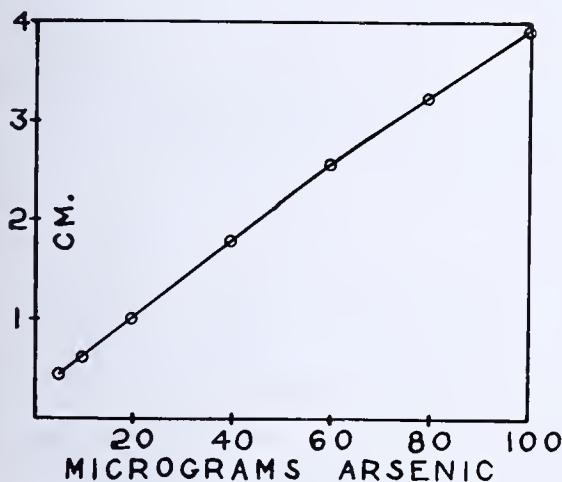


FIGURE 5

Pyrex beads are used to prevent bumping, because a measurable amount of arsenic is dissolved from common beads during the course of an ordinary digestion. It is possible to digest the sample and reduce the arsenic in the tube used as generator, but it is very difficult to prevent bumping when 15 ml. of solution are boiled to remove the sulfur dioxide. A volumetric portion of a stock solution 6 months old was acidified, heated with sodium bisulfite, boiled, diluted, and compared with a similarly treated portion from a freshly made stock solution. Stains produced by like quantities of the two solutions were identical. Such a reduced solution, after standing 3 months, was compared with a freshly reduced portion from the same stock solution. Stains were identical. An attempt was made to use the Gutzeit stick of zinc to displace arsenic from neutral solution. The zinc was then used in a determination with only the low-arsenic reagents. It was possible to detect as little as 0.5γ of arsenic in this way, but the results were too irregular to be of any value in a quantitative procedure.

Since variations of stains could not be correlated with variations of atmospheric pressure, no attempt was made to control the pressure of the gases from the generator as practiced by Bird (10).

Table I is self-explanatory, but attention must be called to the fact that these data were compiled before the extremely pure zinc was acquired, and that the zinc-tin alloy used had an uncontrolled rate of dissolution. The average probable error of graphs drawn from the values in the "average" col-

umn is about 1 per cent for each string. The average probable error of a single determination is for each string slightly less than 2.8 per cent. Adding these values according to the formula  $\sqrt{A^2 + B^2}$  gives an average string probable error of 3 per cent for single determinations of unknowns. Table II shows results obtained through the use of the zinc alloy described under Reagents. Here the error has been further reduced. These data, however, represent constancy of stain lengths and not precision of arsenic determination. Because the straight-line extrapolations of the curves do not pass through the origin, an additional error is involved when stain lengths are transformed into micrograms of arsenic. This becomes serious only in the minimal determinations. Thus the probable error for 0.1γ of arsenic is increased to 5 per cent, but 0.2γ may be estimated with an error of only 3.5 per cent. This decreases to 3.0 per cent for 0.7γ, and reaches a minimum of 1.8 per cent at 1.5γ. The marked change of slope causes an increase of error to 2.2 per cent at 2.5γ and 2.8 per cent at 3.0γ. Similarly, an error of 6 per cent for 5γ by 5 per cent mercuric chloride string drops to 4 per cent for 20γ and to 1.6 per cent for 100γ.

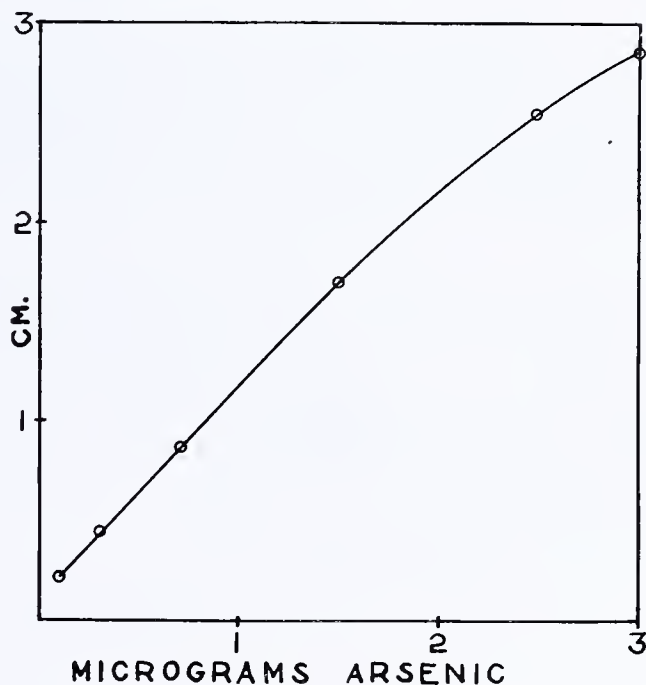


FIGURE 6

Figures 5 and 6 are drawn from the tabulated data on strings 19 and 20, respectively. It will be noted that the curve for string 19 consists essentially of two straight lines, intersecting near the ordinate value that represents a stain length of 2.5 cm. This effect has been noted on other heavily impregnated strings, but is not so marked when the amount of mercuric chloride present is small, as illustrated by Figure 6. Observation of this abrupt change of slope might be of value in a determination of the nature of the stepwise reaction between arsine and mercuric chloride, but an investigation of its possibilities cannot be undertaken in this laboratory.

It has been impossible to eliminate a certain small amount of fading at the termination of the stain. This causes a reading error when measurements are carried to 0.01 cm. The average reading error should not be more than 0.01 cm. and is of little importance when the stain is longer than 1 cm. When a stain shorter than 1 cm. is to be measured, this error may be practically

TABLE II. MICRODETERMINATION OF ARSENIC

String 20, from 0.25 per cent HgCl<sub>2</sub>

String 20, from 0.25 per cent HgCl <sub>2</sub>												P. E. of Av.	P. E. of Single Determination
γ	Length of Stain										Av. Cm.	%	%
	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.			
0.22	0.22	0.22	0.22	0.20	0.20	0.21	0.21	0.22	0.20	0.21	0.95	3.3	
0.43	0.46	0.46	0.47	0.45	0.49	0.45	0.47	0.46	0.43	0.46	0.85	2.6	
0.85	0.84	0.89	0.85	0.83	0.89	0.88	0.88	0.90	0.86	0.87	0.88	2.8	
1.72	1.70	1.66	1.71	1.73	1.66	1.68	1.65	1.70	1.67	1.69	0.48	1.5	
2.60	2.51	2.53	2.52	2.57	2.54	2.52	2.61	2.57	2.51	2.55	0.47	1.5	
2.80	2.91	2.94	2.80	2.84	2.91	2.86	2.82	2.90	2.85	2.86	0.52	1.7	



eliminated by taking the average of a series of about five independent measurements of the length of stain.

Using the very pure zinc alloy, it is possible to detect as little as  $0.01\gamma$  of arsenic. This is shown by string 12 in Figure 7, where 1 shows a blank determination, 2 shows the stain obtained through addition of  $0.01\gamma$ , and 3 represents  $0.05\gamma$  of arsenic. Figure 8 pictures typical 0.1, 0.3, 0.7, 1.5, and  $3.0\gamma$  stains on string 20.



FIGURE 7

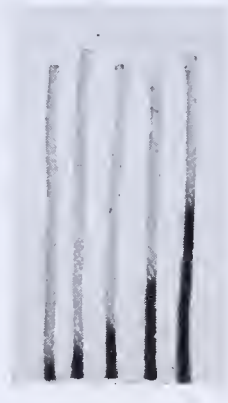


FIGURE 8

Stress has been laid on uniformity—uniformity of reagents, procedure, and apparatus. Since the character of the stain is influenced by nearly every variable in the determination, it is essential for accurate work that strict adherence to standard conditions be observed.

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Courtesy, Leo K. Yanowski and W. A. Hynes

#### VITAMIN C FROM SATURATED AQUEOUS SOLUTION

Original magnification  $\times 120$ . Probably contaminated with oxidation products.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Determination of Columbium and Tantalum in Stainless Steel

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THE addition of columbium to stainless steel to improve its corrosion resistance is increasing rapidly and has necessitated the development of an accurate method for separating this element. Weiss and Landecker (4) state that columbium and tantalum are precipitated from solution by evaporation with perchloric acid. Silverman (3) describes a method for the determination of columbium in 18 per cent chromium-8 per cent nickel steel and in low-titanium steel based on this separation. It has been the author's experience that columbium and tantalum are not quantitatively precipitated by evaporation with perchloric acid when appreciable amounts ( $> 0.10$  per cent) of titanium are present. Furthermore, the columbium that is precipitated is badly contaminated with titanium. Silverman (3) mixed a 1-gram sample of steel containing columbium with 1 gram of 0.30 per cent titanium steel and, because the weight of the final residue, after putting through all of the steps of his method, showed excellent agreement with the weight obtained on direct treatment of the columbium steel alone, concluded that titanium, if present in a columbium steel up to 0.15 per cent, would have no effect on the columbium determination.

The author analyzed a sample of columbium- and titanium-bearing 18 per cent chromium-8 per cent nickel steel by the cupferron method described below, and found 0.83 per cent columbium and 0.45 per cent titanium. A test carried out on this steel by Silverman's (3) procedure gave a final residue which, when analyzed for titanium colorimetrically, showed 0.15 per cent. Lundell, Hoffman, and Bright (1) also point out that titanium interferes with the accurate determination of columbium and tantalum.

In the presence of titanium ( $> 0.1$  per cent), columbium and tantalum may be determined by treating the steel with 200 to 300 ml. of 30 per cent hydrochloric acid at a temperature of approximately  $80^{\circ}\text{C}$ . When the action of the acid has practically ceased, a few drops of hydrofluoric acid are added and the heating is continued for several minutes longer. The solution is cooled to about  $5^{\circ}\text{C}$ ., diluted with cold water to 400 ml., and the columbium, tantalum, and titanium are precipitated by the addition of an excess (20 to 30 ml. are usually sufficient) of a cold, freshly prepared 1 per cent solution of cupferron. Some ashless paper pulp is added, the solution is stirred vigorously for several minutes, filtered on two 1-cm. No. 42 Whatman filler papers (containing some ashless paper pulp) supported on a Büchner funnel, gentle suction being employed, and the paper and precipitate are washed at least 20 times with cold 10 per cent hydrochloric acid containing 20 ml. of the cupferron solution per liter. The paper is ignited in a 100-ml. platinum dish at a low temperature, fused with 3 to 5 grams of potassium pyrosulfate, and the melt, when cool, is dissolved in 200 ml. of 5 per cent tartaric acid containing 4 ml. of

sulfuric acid (1 to 1). The solution is then treated with a brisk stream of hydrogen sulfide for 15 to 20 minutes. If a precipitate forms it is filtered on a 9-cm. paper containing some ashless paper pulp, washed 18 to 20 times with hydrogen sulfide water containing 0.5 per cent sulfuric acid and 5 per cent tartaric acid, and discarded.

An excess of about 2 ml. of ammonia (sp. gr. 0.90) is added and the solution is treated with hydrogen sulfide for 5 minutes longer. Some ashless paper pulp is introduced and after the precipitate of ferrous sulfide has been allowed to digest at a temperature of approximately  $70^{\circ}\text{C}$ . for 10 minutes, it is filtered, washed well with ammonium sulfide water containing 2 per cent ammonium chloride and 2 per cent tartrate, and discarded. The filtrate is boiled to expel hydrogen sulfide, 40 ml. of hydrochloric acid (sp. gr. 1.19) are added, and the boiling is continued until the volume has been reduced to about 300 ml. The solution is cooled to  $15^{\circ}\text{C}$ . and the columbium, tantalum, and titanium are precipitated with cupferron, filtered, and washed as previously described. The precipitate is ignited first at a low temperature and finally at  $1000^{\circ}$  to  $1050^{\circ}\text{C}$ ., cooled, and weighed. The ignited and weighed precipitate is fused with about 12 times its weight of potassium pyrosulfate, the melt is dissolved in 100 ml. of 20 per cent sulfuric acid containing 1 gram of succinic acid and 1 ml. of 30 per cent hydrogen peroxide, and the titanium is determined colorimetrically. Then, 25 ml. of a 20 per cent sulfuric acid solution (containing 0.0500 gram of pure titanium dioxide fused with 2 to 3 grams of potassium pyrosulfate) are added and the columbium in the solution is estimated by the procedure described in the method given below.

Commercial columbium steels are essentially free from titanium; therefore, the determination may be carried out as described in the method. However, in case of doubt, the cupferron method should be used.

The total oxides of columbium and tantalum found on a sample of 18 per cent chromium-8 per cent nickel steel by the method described below showed excellent agreement with the total oxides obtained by this cupferron method. The proposed method can also be worked in considerably less time than the cupferron method.

The tantalum content of the total oxides obtained on a 10-gram sample of columbium-bearing 18 per cent chromium-8 per cent nickel steel can be obtained by the author's modification of Schoeller and Powell's (2) tannin procedure.

For this separation the precipitate is fused with 12 times its weight of potassium pyrosulfate and the melt, when cool, is dissolved in 100 ml. of hot 2 per cent ammonium oxalate. The solution is treated with 2 ml. of sulfuric acid (1 to 1), diluted to 250 ml. with hot water, and heated to boiling. Four drops of a 0.25 per cent solution of bromophenol blue (prepared by dissolving 0.25 gram of the indicator in 7.5 ml. of 0.05 *N* sodium hydroxide and diluting with cold water to 100 ml.) are added, followed by ammonia (1 to 2) drop by drop until the yellow color just



TABLE I. TESTS MADE ON COLUMBIUM-TREATED 18 PER CENT CHROMIUM-8 PER CENT NICKEL STEEL

Sample	Sample Taken Grams	Total $\text{Cb}_2\text{O}_5$ + $\text{Ta}_2\text{O}_5$ Found Gram		Total $\text{Cb}_2\text{O}_5$ + $\text{Ta}_2\text{O}_5$ Gram			Tannin Procedure		
							Total $\text{Cb}_2\text{O}_5$ + $\text{Ta}_2\text{O}_5$ Gram	Cb %	Ta %
38	3	0.0421	0.980	.....	.....	.....	.....	.....	.....
38	5	0.0705	0.986	0.0705	0.934	0.06	0.0700	0.932	0.058
38	2	0.0280	0.980	.....	.....	.....	.....	.....	.....
38	2	0.0282 <sup>c</sup>	0.986	.....	.....	.....	.....	.....	.....
123	5	0.0320 <sup>c</sup>	0.45	0.0320	0.426	0.029	.....	.....	.....
123	10	.....	.....	.....	.....	.....	0.0640	0.429	0.026
123	15	.....	.....	.....	.....	.....	0.0960	0.424	0.027
123	5	.....	.....	0.0320	0.426	0.029	.....	.....	.....

<sup>a</sup> Per cent total oxides found calculated to columbium.<sup>b</sup> Results obtained by addition of  $\text{TiO}_2$ , fusion with  $\text{K}_2\text{S}_2\text{O}_7$ , and passing the solution through the reductor as described in the method.<sup>c</sup> Result obtained by cupferron method.

changes to a distinct purple. This corresponds to a pH of approximately 4.6. From 25 to 30 ml. of a freshly prepared 1 per cent solution of tannin are added, followed by 10 grams of ammonium chloride and some ashless paper pulp, and the solution is gently boiled for at least 15 minutes.

The hot solution is filtered on an 11-cm. paper containing some ashless paper pulp, and the paper and precipitate are washed from 20 to 25 times with a hot 2 per cent solution of ammonium chloride and ignited in platinum at a low temperature to burn off the carbon of the filter paper. The precipitate is treated in platinum with 5 ml. of sulfuric acid (1 to 1) and 1 ml. of hydrofluoric acid, and the solution is evaporated to a volume of 1.5 to 2 ml., cooled, and transferred to a 250-ml. beaker by means of 150 ml. of cold 2 per cent hydrochloric acid. Twenty-five milliliters of sulfurous acid and some ashless paper pulp are introduced, the solution is boiled for at least 5 minutes, and allowed to stand for 30 minutes or longer at about 70° C. before filtering. The precipitate is ignited and weighed. A weight of 0.0200 gram of pure titanium dioxide is added, the mixture is fused with 12 times its weight of potassium pyrosulfate and the melt is dissolved as described in paragraph 3 of the method. The solution is passed through the reductor and titrated with standard 0.05 *N* potassium permanganate, all as described in paragraphs 4 and 5 of the method. A blank on the reductor and titanium dioxide is carried through as described and the difference in volume of permanganate between the sample and the blank is the volume equivalent to any  $\text{Cb}_2\text{O}_5$ . The weight of  $\text{Ta}_2\text{O}_5$  (+  $\text{Cb}_2\text{O}_5$ ) less the  $\text{Cb}_2\text{O}_5$  found, multiplied by 81.91 and divided by the weight of sample taken, gives the percentage of tantalum.

Tantalum oxide is white whether hot or cold, whereas columbium oxide is yellow when hot and white when cold. Silverman (3) states that  $\text{Cb}_2\text{O}_5$  is nearly white when cold, which would indicate that his oxide was impure. In order to remove silica and to purify the precipitate obtained by evaporation with perchloric acid, it is ignited and treated with hydrofluoric, sulfuric, and perchloric acids, finally evaporating the solution to dense fumes of sulfuric acid. The columbium and tantalum in this solution are then precipitated by boiling with sulfurous acid, filtered, ignited, and weighed as oxides.

The following method has, with but few modifications, been used by this laboratory since 1932 and by other laboratories since 1933, and requires about 2.5 hours.

### Method

From 2 to 5 grams of the sample are transferred to a 600-ml. covered beaker and treated with from 25 to 50 ml. of hydrochloric acid (sp. gr. 1.19) and 10 ml. of nitric acid (sp. gr. 1.42) at a temperature of approximately 90° C. When all action appears to have ceased, 30 to 60 ml. of perchloric acid (60 per cent) are introduced, the solution is boiled until dense fumes of perchloric acid are freely evolved, and the boiling is continued for about 5 minutes longer to ensure the complete conversion of the chromium to chromic acid. Two hundred milliliters of hot water, 50 to 100 ml. of sulfurous acid, and 10 ml. of hydrochloric acid (sp. gr. 1.19) are introduced and the solution is boiled for 5 minutes. Considerable ashless paper pulp is introduced, and the contents of the beaker are allowed to digest at a temperature of from 60° to 70° C. for 15 minutes, or until the supernatant liquid is clear,

and filtered on an 11-cm. paper containing some ashless paper pulp. The beaker is scrubbed with a filter paper moistened with 2 per cent hydrochloric acid and added to the filter. The paper and precipitate are washed from 12 to 15 times with hot 2 per cent hydrochloric acid and ignited in a 50-ml. platinum dish at a low temperature to burn off the carbon of the filter paper.

Approximately 5 ml. of hydrofluoric acid (48 per cent) and 10 ml. of sulfuric acid (1 to 1) are introduced, the solution is evaporated to dense fumes of sulfur trioxide, and the fuming is continued until the volume has been reduced to approximately 2.5 ml. to ensure the complete expulsion of all hydrofluoric acid. Should the precipitate not dissolve after several minutes' heating, approximately 2 ml. of perchloric acid (60 per cent) are added and the solution is evaporated as described. If the

evaporation is allowed to proceed almost to dryness, any separated columbic or tantallic acids may be dissolved by the addition of several milliliters of sulfuric acid (sp. gr. 1.84) and further heating for 1 or 2 minutes. The contents of the dish are allowed to cool somewhat and transferred to a 400-ml. beaker by means of about 200 ml. of hot 2 per cent hydrochloric acid. Any adhering precipitate is removed from the dish by means of an 11-cm. filter paper moistened with hydrochloric acid, and added to the beaker. An excess (about 50 ml.) sulfurous acid is added, and the solution is boiled for 5 minutes. Some ashless paper pulp is introduced, and the solution is digested at a temperature of from 60° to 70° C. for 15 minutes, or until the supernatant liquid is clear, filtered on an 11-cm. paper containing some ashless paper pulp, and washed 10 times with hot 2 per cent hydrochloric acid. The precipitate is ignited in a 50-ml. platinum dish, first at a low temperature to burn off the carbon of the filter paper, and finally to constant weight at 1000° to 1050° C., cooled, and weighed. (For a control analysis, the weight obtained multiplied by 69.9 and divided by the weight of sample taken, will give the approximate percentage of columbium.)

To the ignited and weighed precipitate of columbium and tantalum oxides is added 0.0500 gram of pure titanium dioxide, and the mixture is fused with 2 to 3 grams of potassium pyrosulfate. The dish and its contents are permitted to cool somewhat, 5 ml. of sulfuric acid (sp. gr. 1.84) are introduced, and the heating is continued on a hot plate until a clear solution is obtained. The contents of the dish are allowed to cool partially, are transferred to a dry 250-ml. beaker, and the dish is rinsed successively with three 5-ml. portions of sulfuric acid (sp. gr. 1.84). The dish is further rinsed with 20 ml. of 5 per cent succinic acid containing 1 ml. of 30 per cent hydrogen peroxide, and the rinsings are added to the beaker. The solution is stirred thoroughly, diluted to 100 ml. with cold water, heated to 60° to 70° C., passed through a Jones reductor into a solution of ferric sulfate, and titrated with a standard solution of potassium permanganate. The columbium and titanium are reduced from  $\text{Cb}_2(\text{SO}_4)_3$  and  $\text{Ti}(\text{SO}_4)_2$  to  $\text{Cb}_2(\text{SO}_4)_3$  and  $\text{Ti}_2(\text{SO}_4)_3$ , respectively, whereas the tantalum is not affected. The titanium added serves to prevent hydrolysis of the columbium and tantalum in the reductor. The columbous and titanous sulfates immediately react with the ferric sulfate to form  $\text{Cb}_2(\text{SO}_4)_3$  and  $\text{Ti}(\text{SO}_4)_2$ , respectively, and a corresponding amount of ferrous sulfate equivalent to the reduced columbium and titanium.

A Jones reductor having a column of 20-mesh zinc 75 cm. (30 inches) long is required. The zinc should be amalgamated by treating 800 grams, of very low iron content, with 400 ml. of a 2.5 per cent mercuric chloride solution in an 800-ml. beaker and stirring vigorously for 2 minutes. The solution is decanted off and the zinc washed with water, transferred to the 75-cm. (30-inch) reductor, and further washed with hot 2.5 per cent sulfuric acid and water. The reductor, filled with amalgamated zinc as described, is good for about 6 determinations, when it should be emptied and filled with new zinc freshly amalgamated. Immediately before using the reductor it is well to pass through it 200 ml. of almost boiling water in order to preheat the column of zinc. The reductor is then connected to a 1000-ml. suction flask with the delivery tube dipping beneath the surface of 25 ml. of ferric sulfate solution (prepared by dissolving 100 grams of ferric sulfate in a solution containing 150 ml. of phosphoric acid, sp. gr. 1.72, 20 ml. of 1 to 1 sulfuric acid, and 850 ml. of water), and the following solutions are passed through it in the order named: 100 ml. of hot (60° to 70° C.) 20 per cent sulfuric acid; the columbium solution, also heated to 60° to 70° C.; 100 ml. of hot (60° to 70° C.) 20 per cent sulfuric acid containing 1 gram of dis-



solved succinic acid; and three 50-ml. portions of cold water. At no time is the funnel that forms the reductor inlet permitted to become entirely empty, and the reductor when idle should always be kept full of distilled water to above the top of the zinc.

The solution is cooled to room temperature by addition of several ice cubes prepared from distilled water, transferred to an 800-ml. beaker, and titrated with 0.05 *N* potassium permanganate solution (1 ml. is equivalent to 0.002323 gram of columbium or 0.002395 gram of titanium) that has been standardized against sodium oxalate from the Bureau of Standards. A "blank" on the reagents and reductor is made by fusing a 0.0500-gram portion of pure titanium dioxide with 2 to 3 grams of potassium pyrosulfate (the same amount used in the analysis), dissolving the melt, and passing it through the Jones reductor, all as described in the third and fourth paragraphs. The solution is cooled to room temperature and titrated with 0.05 *N* potassium permanganate. The total volume of standard 0.05 *N* potassium permanganate solution required, less the "blank" (including 0.0500 gram of titanium dioxide) is multiplied by 0.002323 and divided by the weight of sample taken to give the per cent of columbium. The weight of columbium found is multiplied by 1.43 to give the corresponding weight of columbium pentoxide. The weight of the total oxides of columbium and tantalum obtained as described in the second paragraph, less the weight of columbium pentoxide found, gives the weight of tantalum pentoxide, which, multiplied by 81.91 and divided by the weight of sample taken, gives the percentage of tantalum in the steel.

A modification of this method is necessary for steels containing molybdenum and tungsten. When titanium is present in amounts greater than 0.10 per cent, it is necessary to use the cupferron method described above.

If desired, the ignited and weighed precipitate of columbium

and tantalum pentoxides, obtained as described in the second paragraph, may be fused with potassium pyrosulfate without any titanium dioxide addition, the melt dissolved as described in the third paragraph, and the solution passed through the reductor, cooled, and titrated, all as described in the fourth and fifth paragraphs of the method. A "blank" in this case is run on the reductor by dissolving 2 to 3 grams of potassium pyrosulfate in 100 ml. of 20 per cent sulfuric acid containing the same amounts of succinic acid and hydrogen peroxide that were used in the analysis, and putting the solution through the reductor as described, cooling, and titrating. It is very difficult to obtain complete reduction of columbium by means of a Jones reductor (unless titanium is added) but, if the directions given are closely followed, the reduction is so nearly complete that the error thus introduced is not significant when dealing with the amount of columbium usually found in a sample of steel.

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## Accurate Determination of Dew Point

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**The apparatus features sensitive instrumental observation of dew, combined with minimization of systematic errors in the measurement of the temperature at the gas-liquid interface.**

**The technic is such as to eliminate the marked hysteresis error characteristic of methods involving continuous temperature change. An accuracy of  $\pm 0.01^\circ$  C. is reached.**

**A double gaseous film adjacent to the liquid phase is hypothesized in explanation of observed phenomena.**

**D**IRECT dew-point determination affords a sensitive means of determining vapor concentrations. The formation of dew has been utilized as a criterion in the investigation of phase equilibria with reference to motor fuels (2, 6, 12) and hydrocarbon systems under pressure (8, 9). Improvement in the accuracy of dew-point indication should increase its usefulness as a research tool.

Reviews of hygrometric methods (10, 11) indicate that the means of dew-point determination used in 1916 offered little advantage in dependability over the ether-cooled silver mirror of Regnault (?). The accuracy of preferred forms of apparatus varied from  $0.2^\circ$  to  $2^\circ$  C. with decrease in relative humidity.

It appears that these errors were due largely to the unmeasured temperature gradient between the gas-liquid interface and the temperature-recording device. This temperature gradient has two components: (1) the drop across the dew itself, and (2) the drop within the apparatus.

Griffiths (1) reduced the second component by inserting the thermometer in a metal block upon whose surface the dew deposited. Readings at appearance and disappearance of dew differed by  $0.1^\circ$  to  $2.2^\circ$  C. Holtzmann (3) accomplished virtual elimination of the second component by use of a thermocouple mounted close to the metal deposition surface. An ingenious technic of observation yielded a precision (reproducibility) of some  $0.03^\circ$  C., dependent upon the experience and skill of the observer. Accuracy was not established, results differing from psychrometer readings by the equivalent of some  $0.1^\circ$  C. variation in dew point. It is to be noted especially that this method must be classified among those depending upon the presence at the dew point of sufficient dew to be detected with certainty by visual means. This would cause error in determinations on confined systems, through coincident decrease of vapor concentration in the sample whose composition is sought.

Dew indication through alteration in surface resistance was investigated by Johnstone (4) and Tchang (13). The ease of visual observation of dew deposit was improved by the use of a platinum-blackened surface by Stevenson and Babor (12), who applied their method to the study of the volatility of gasoline. Sage and Lacey (8, 9) applied a modification of the dew-point method to the investigation of phase equilibria in hydrocarbon mixtures. In this case dew was detected through thermal effects caused by the formation of a single hanging droplet 0.1 mm. in diameter. It is again noted that formation

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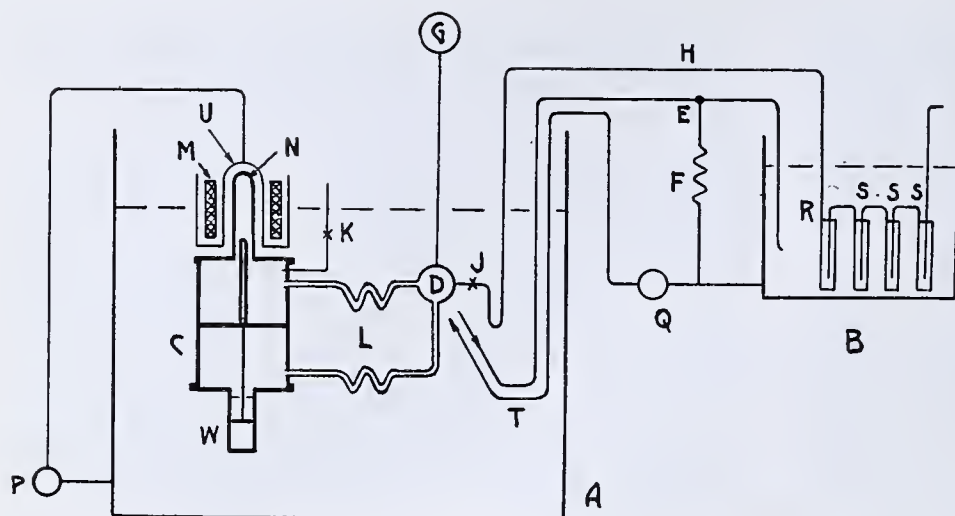


FIGURE 1. APPARATUS FOR INVESTIGATION OF DEW DEPOSITION

of such an amount of liquid occasions change in the composition of the gaseous phase. Tomlinson (14) made use of a photoelectric method for detection only, an arbitrarily selected quantity of dew deposit causing actuation, through amplifier and relay, of a signal lamp.

None of these methods succeeded in producing a satisfactory reduction of the first component of the temperature gradient error previously mentioned. This might be accomplished by a method in which the amount of dew approached zero at the dew point. Such a method could be applied to confined systems without introducing further error through depletion of vapor in the gaseous phase. Requirements include extreme sensitivity coupled with a technic of continuous quantitative estimation of variation in dew quantity in the temperature range near the dew point. The apparatus described below was designed to meet these requirements.

### Method

Accurate direct determination of the dew point of confined samples is accomplished through a sensitive photoelectric means of dew observation, combined with a technic of intermittent temperature rise calculated to minimize the quantity of dew present at the time the deposition surface reaches the dew-point temperature.

### Apparatus

Figure 1 is a diagrammatic representation of the apparatus, whose design included provision for operation above atmospheric pressure.

In thermostat *A* is the dew chamber, *D*, through which a periodically reversed circulation of the gas body is maintained by the 10.2-cm. (4-inch) stroke of a brass piston 12.7 cm. (5 inches) in diameter moving in a steel cylinder, *C*. The connecting coils, *L*, each composed of 0.9 meter (3 feet) of tubing 1.3 cm. (0.5 inch) in diameter, provide added surface for the maintenance of constant and uniform temperature of the gas. The Bourdon pressure gage, *G*, is connected with chamber *D* through an oil- and mercury-filled loop to minimize dead-end space. Bath temperature is measured by a calibrated thermometer graduated in  $0.1^{\circ}\text{C}$ .

For introduction of a sample, gas is passed through Milligan saturators *S*, cotton-packed spray catcher *R*, heated vapor line *H*, valve *J*, chamber *D*, coils *L*, and cylinder *C* to outlet valve *K*, the piston being in operation during the process.

**MAGNETICALLY OPERATED PISTON.** The circulating piston is raised by the fan-cooled solenoid, *M*, contained in the thermally insulated brass can, *U*. The brass cylinder extension, *N*, is bathed in water circulated from thermostat *A* by gear pump *P* through an insulated pipe. The rate of rise of the piston is controlled by an attached auxiliary piston working in mercury well *W*, displacement of mercury occurring through channels controlled by needle valves situated within the apparatus. Rise of piston was set to about 1 minute, fall requiring 2 minutes. A motor-driven mercury switch controls the solenoid operating cycle, which totals 3.6 minutes.

**DEW-MIRROR TEMPERATURE.** The temperature of the dew mirror is controlled by circulation of water from thermostat *B* through pump *Q* and insulated lines *T*. Temperature of thermostat *B* is measured by a thermometer similar to that used in the large bath. For easier and more reliable readings of temperature intervals, a Beckman graduated to  $0.01^{\circ}\text{C}$ . is also employed. Rapid chilling of mirror for initial dew deposition is effected by use of cock *E* and water-cooled coils *F*.

Figure 2 shows the submerged dew chamber, in which is the mirror, *M*, of diameter 1.27 cm. (0.5 inch). The flow of the sample is directed horizontally across and immediately adjacent to this mirror. The mirror is integral with the brass billet, *C*, which is thermally insulated by means of Bakelite disks *B* and plastic insulation *I*. Two holes were drilled through the billet at *M*, and countersunk. The enameled thermocouple wires, *W*, were brought up through these holes and fastened by filling the countersinks with solder. Surface *M* was then polished and chromium-plated in order to assist the deposition of dew in the form of many discrete droplets. The actual thermocouple junction is 0.8 mm. (0.03 inch) below mirror *M*. The temperature difference between these two points is calculated to be less than  $0.01^{\circ}\text{C}$ . when the mirror is  $50^{\circ}\text{C}$ . below the temperature of the gas body.

The copper-constantan thermocouple wire, specially drawn, was tested for inhomogeneity, insulated with fine rubber tube, and enclosed in a flexible waterproof metal conduit, which formed part of the interconnected equipotential shield protecting the entire measuring circuit from leakage currents. The cold junction is in thermostat *B*. The couple thus serves to measure merely the temperature drop along the water-circulating system, and is directly connected through an all-copper circuit with a sensitive

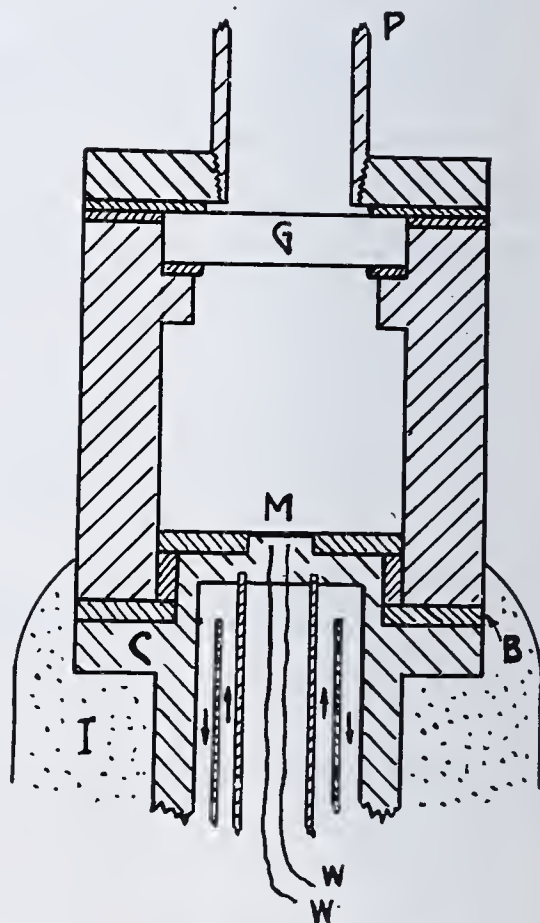


FIGURE 2. DEW CHAMBER

galvanometer. Before the billet, *C*, was bolted into place, the thermocouple and galvanometer set-up was calibrated directly against carefully compared Beckman thermometers, yielding a mean value  $0.023^{\circ}\text{C}$ . per mm. of scale deflection. From the temperature of bath *B*, the mirror temperature can thus be calculated.

**OPTICAL SYSTEM.** The source of light is a concentrated filament storage battery lamp. The parallel beam produced by a



collimating system passes through an infrared filter and is reflected down along one side of pipe *P* through window *G* to a small total reflecting prism. From this prism the beam reaches the mirror at an angle of some  $10^\circ$  to its surface, and thence, by means of a second reflecting prism, is made to travel back up the other side of pipe *P* to be reflected to a sensitive photoelectric cell.

Owing to the small angle between the incident beam and the mirror surface, the large number of discrete dew droplets intercept and disperse a large fraction of the light, increasing the sensitivity of dew detection.

**AMPLIFIER.** The photoelectric cell controls the grid circuit of a three-element vacuum-tube amplifier. To attain satisfactory constancy of operating conditions, heavy-duty B-batteries are used in conjunction with a storage A-battery. Plate current is read to 0.02 ma. Drift is determined before and after each run.

## Results

A series of preliminary investigations indicated that a gradual decrease in light transmission occurs with decrease in mirror temperature, even when the latter remains well above the dew point. No such effect was noted when the apparatus was evacuated, nor when it was filled with dried air. It appears that the apparatus is sufficiently sensitive to register the presence of gaseous films adjacent to the mirror, of composition differing somewhat from the body of gas due to localized cooling at nearly constant pressure.

### CONTINUOUS TEMPERATURE CHANGE.

For slow cooling, the plot of plate current versus mirror temperature showed no sharp break, but changed direction gradually over a range of several tenths of a degree. Determination on falling temperature was discarded in favor of a slow temperature rise following preliminary deposition of dew.

Plot 1, Figure 3, illustrates the form of graph obtained through runs by the latter method. There are two breaks, the less distinct lower break, *L*, and the sharp upper break which no doubt would be the only one observable by direct visual means. However, in runs on the same sample at a heating rate of about  $0.004^\circ \text{C.}$  per minute, the lower breaks checked one another within  $0.01^\circ \text{C.}$ , while the upper breaks differed by over  $0.1^\circ \text{C.}$  Varying the heating rate from  $0.004^\circ \text{C.}$  per minute in one run to  $0.014^\circ \text{C.}$  per minute in another, the discrepancy between upper breaks increased to  $0.2^\circ \text{C.}$ , while the lower breaks again checked each other. It appears that the lower break, not the upper one, corresponds to the true dew point. Unfortunately, the lower break is poorly defined.

**INTERMITTENT TEMPERATURE CHANGE.** To eliminate the effect of dew evaporation with rising temperature, further runs were conducted in a stepwise manner. After preliminary deposition of dew, the rise was accomplished by rapid heating through suitable small temperature intervals, in each case maintaining temperature at the new level until plate current became constant, the criterion of the latter being in most cases a maximum change of about 0.04 milliamperes per cycle (3.6 minutes). The final reading of plate current, in each series, was plotted against temperature.

Four such determinations checked within an extreme range of  $0.02^\circ \text{C.}$ , the plots consisting of two well-defined intersecting straight lines. In two of these runs the point nearest the intersection fell off the lines. This defect was remedied by extrapolating to infinite time (zero rate of plate

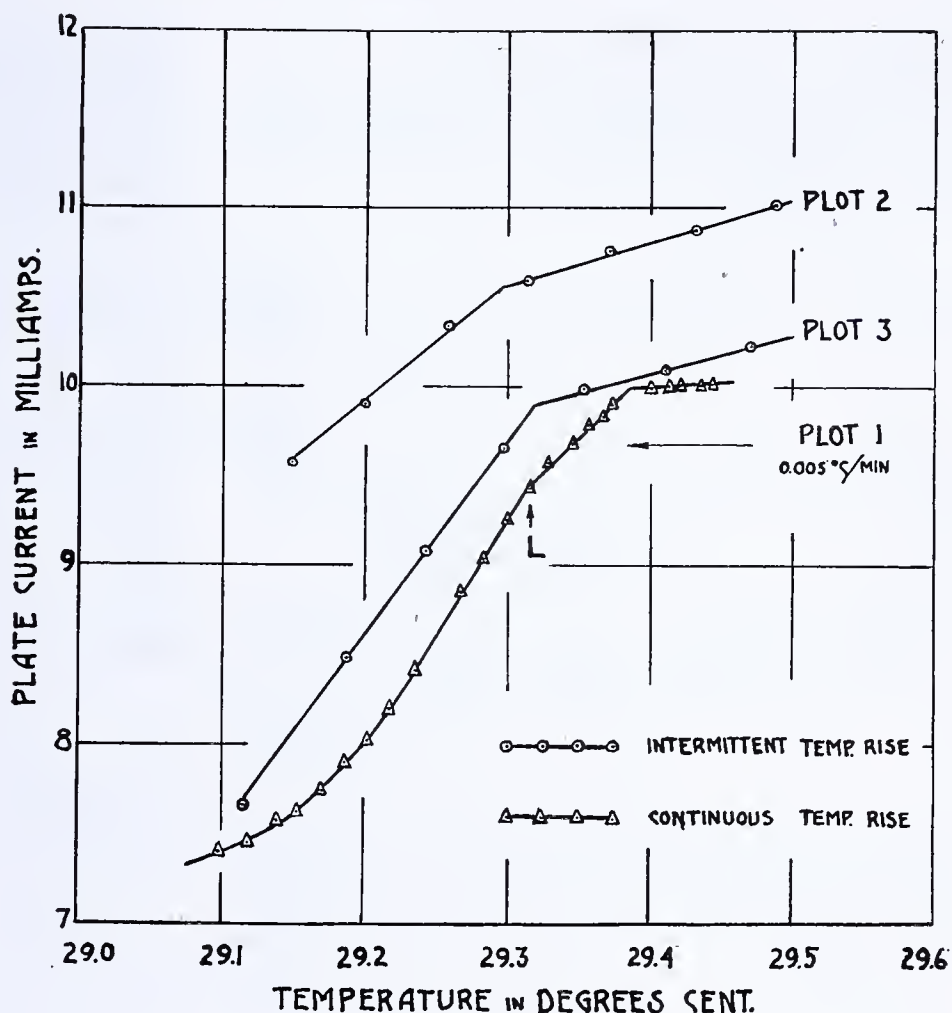


FIGURE 3. COMPARISON OF TECHNIQUES OF DETERMINATION

current change) each series of observations at a given temperature. Plots 2 and 3, Figure 3, drawn from the extrapolated values, also agree within  $0.02^\circ \text{C.}$  Moreover, no readable difference in dew point resulted, in either case, from use of extrapolated instead of final readings. It appears that the work of extrapolation may be omitted.

**COMPARISON OF TECHNIQUES.** Determinations represented in Figure 3 were all on the same sample, of about 90 per cent relative humidity. It now seems clear that the break, *L*, of plot 1 is to be identified with the true dew point as determined by plots 2 and 3.

The intermittent rise method presents advantages of improved sensitivity and superior convenience. Its success depends upon the use of sensitive instrumental observation, such as the photoelectric system herein described.

**SATURATED SAMPLES.** The means leading to precision of dew-point determination having been investigated, it was desired to discover if the accuracy attainable was of comparable degree. It was found impossible to introduce into the apparatus a prepared partially saturated sample without change in composition far greater than the precision of the determination. It was accordingly decided to work with saturated samples, prepared by introduction of water directly into the tubes connecting cylinder with dew chamber.

The continuous rise method produced in this case no definite break in the plotted results, but the intermittent rise technic yielded the plots of Figure 4. Letters *D* indicate the dew points of the respective samples, calculated to the temperature scale plotted by consideration of thermometer corrections and reading of the differential galvanometer. Letters *B* indicate the observed breaks. *B* and *D* differ in each case by some  $0.04^\circ \text{C.}$  There is uncertainty as to the exact point of intersection, occasioned by the relatively great angle between the component sections of each plot. It is thus to be expected



that a corresponding divergence from absolute values would be noted.

While sensitivity, precision, and accuracy do not here measure up to the precision noted on unsaturated samples, these runs do serve definitely to indicate that the break in question corresponds to the true dew point.

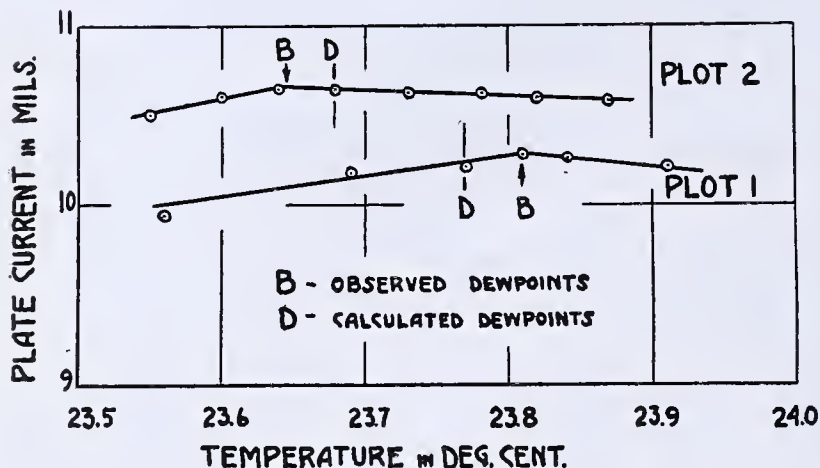


FIGURE 4. DETERMINATIONS ON SATURATED AIR

**VARIATIONS IN TECHNIC.** The objection might be advanced that absorption of infrared rays by the dew could have affected the observations. The infrared filter first used was simply a water cell. Replacement of the water by a 2 per cent solution of cupric chloride produced no apparent change in the final results. In some runs, the light beam was blocked completely, except during periods of observation, without noticeable change in indications.

No improvement resulted from coating the mirror with platinum black (12), suspending gas circulation, or varying the rate of transition between test temperatures.

### Discussion

The data give rise to a number of questions concerning the mechanism through which occurs the interchange between liquid and gaseous phases. Chief among these are:

1. Equilibrium when mirror is below the dew point. During intermittent rise runs it was observed, at each temperature level, that the light transmission became greater than that at the preceding level, but slowly approached constancy. From usual considerations, it would be expected that dew would deposit on, rather than evaporate from, a surface remaining at a temperature below the dew point.
2. Break in plot for unsaturated samples, intermittent rise runs. An explanation is needed for the abrupt change in slope. Note that since these were equilibrium readings, no rates of evaporation or diffusion are involved.
3. Break in plot for saturated samples, intermittent rise runs. Why is the change in slope less than in the case of unsaturated samples?
4. Breaks in plots for unsaturated samples, continuous rise runs. Why is the lower break lacking in sharpness? What is the significance of the upper break, and why does its position vary widely in runs under different conditions of dew and heating rate?

In correlating these ideas, it should be borne in mind that the amount of light transmitted to the photocell is affected by changes in the gaseous phase as well as in the liquid phase. Such changes may include convection currents or the formation of films of varying thickness and vapor content. They may partially deflect the light beam from its normal course through mirror and aperture system, or alter its intensity by absorption. It is also to be remembered that the temperature gradient, between the dew mirror and the body of the gaseous phase, will be largely across the gas film rather than the liquid.

**DOUBLE-FILM HYPOTHESIS.** To coordinate the observed qualitative and quantitative data the double-film hypothesis

is advanced. This concept is in accord with accepted physical laws governing behavior of gases and vapors. Figure 5 presents temperature and vapor concentration gradients in the thin films immediately adjacent to the surface of the deposited liquid. The precise form of the plots, between the lettered points, is not material to the development of the concept.

Consider a general case, wherein a liquid surface is at a temperature  $T'$  below the dew point of a body of vapor-gas of temperature  $T_g$  and vapor concentration  $A$ , less than saturation. The temperature gradient causes a corresponding density gradient, producing a stratification in the gas phase immediately adjacent to the liquid. This will be most marked when the liquid surface is horizontal and there is but little circulation in the gas phase, but will probably exist to lesser degree in absence of either of these conditions. In the diagram, the range above  $T_g$  and  $A$  is that wherein circulation maintains approximate uniformity in composition and temperature of the gas phase.

Approaching the liquid-gas interface, the temperature declines. The first effect of this, indicated by section  $AB$  of the concentration line, is to increase vapor concentration, since this localized cooling is at essentially constant pressure. The film so produced is still unsaturated, until with decreasing temperature and increasing vapor concentration, saturation is reached at concentration  $B$  and temperature  $T$ . This temperature  $T$  is the true dew point.

The liquid surface is at a still lower temperature,  $T'$ , and the gas in direct contact with it has a vapor concentration  $C$ , which is lower than  $B$ , owing to condensation of liquid from the gas phase. Thus there must exist between points  $B$  and  $C$  a saturated film, across which there is a concentration gradient as well as a temperature gradient. Keevil and Lewis (5) discussed a comparable condition in connection with the dehumidification of air, but omitted consideration of the unsaturated film  $AB$ . In the present instance, a steady state exists at each test temperature, without transfer of vapor across the double film. If the system reached this state by prior lowering of the liquid surface from a higher temperature, the saturated film may contain, suspended in it, a fog of liquid droplets, whose source was the condensation above mentioned.

Were the original vapor-gas mixture saturated, there would be no unsaturated film. The temperature gradient,  $T_g T$ , and the concentration gradient,  $AB$ , would become zero. The character of the saturated film would remain as indicated in the diagram.

**CORRELATION WITH THE DATA.** From the standpoint of the concept above developed, the major questions raised by the experimental data can now be answered.

1. Equilibrium when mirror is below the dew point. The above concept makes it clear that the liquid surface is in equilibrium with a gas carrying vapor concentration  $C$ , Figure 5. This concentration may be less than that in the body of the gas, owing to prior condensation within the saturated film. Hence for each mirror temperature, an equilibrium condition may be established, even though the mirror is below the dew point.
2. Break in plot for unsaturated samples, intermittent rise runs. Referring again to Figure 5, if the temperature of the liquid surface be raised through a small interval, and held at the new level, a readjustment of both films may be expected to occur. Changes will involve temperature gradients, concentration gradients, and thicknesses, the general relationships remaining as before, so long as  $T'$  is still below the true dew point  $T$ . Changes in light reflection between temperature levels are represented by the left section of, for example, plot 2, Figure 3. These changes are affected also by alterations in amount of dew on the mirror. When  $T'$  is raised to coincide with  $T$ , there is no longer a saturated film, nor will the liquid phase persist above this temperature. Further temperature increase causes variations in the remaining single unsaturated film, represented by the right section of plot 2, Figure 3. The abrupt change of slope is a consequence of the abrupt change in physical nature of the entities affecting the transmission of the light. Another break might be expected if  $T'$  were raised high enough to coincide with  $T_g$ , the temperature of the gaseous body, at which point the unsaturated film would in turn disappear.
3. Break in plot for saturated samples, intermittent rise runs. In this case there is at no point an unsaturated film. The cause of the breaks in the plots, Figure 4, is entirely different from that discussed in the preceding paragraph in connection with un-



saturated samples. In saturated samples, the transition is from a condition wherein there is present a saturated film of varying thickness, to one wherein there is no film of this character. When  $T'$  becomes greater than  $T_g$  slight convection currents may be set up, whose disturbance of light transmission is, in part, the cause of the negative slopes of the right sections of the plots in Figure 4. Definite indication of the existence and effect of such convection currents has been noted. With rapid continuous heating of the mirror, in the absence of dew, sudden drops in light transmission occurred when mirror temperature exceeded the temperature of the gas body by some  $0.1^\circ\text{C}$ .

4. Breaks in plots for unsaturated samples, continuous rise runs. The lack of sharpness in the lower break of, for example, plot 1, Figure 4, may be attributed to disturbances arising from irregular convection currents. Such currents are caused by the relatively rapid and continuous rise of the temperature of the dew surface. Temperature gradients set during such a rise are the reverse of those existing in the double film at equilibrium, and, time being insufficient to allow their dissipation through conduction or readjustment of the film, a convection overturn occurs. The upper break is thought to arise from a still different source from those previously discussed, in this case corresponding to the completion of the processes which, were it not for the hysteresis introduced by the continual variation in temperature, would have been completed at the lower break. The wide divergence in upper breaks in different runs reflects different values of this hysteresis, brought about by variation in amounts of dew originally deposited, and by variation in the heating rates.

**DETERMINATION AT OTHER HUMIDITIES.** In determinations of dew point by usual means, error increases with lowered humidity. This is due primarily to the augmented temperature gradient between the body of vapor-gas and the temperature-measuring device. As set forth in the discussion of design of apparatus, this causes error in two ways.

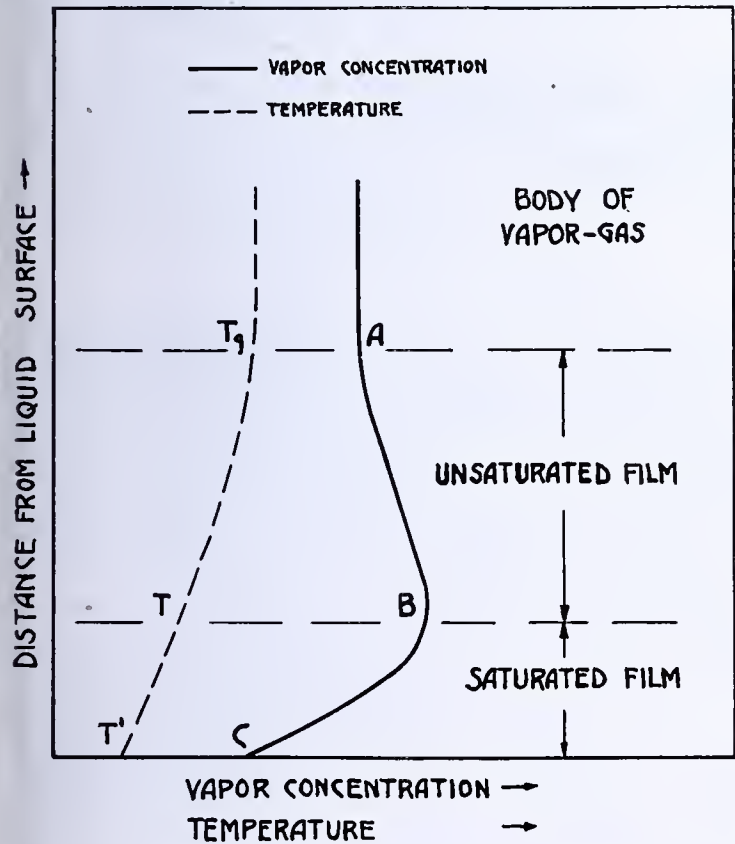


FIGURE 5. MECHANISM OF PHASE CHANGE

In the present apparatus, error due to temperature gradient between thermocouple and mirror surface has been reduced to an estimated  $0.01^\circ\text{C}$ . for a  $50^\circ$  differential between temperatures of sample and dew-point mirror. Error due to temperature gradient across the dew film is eliminated by two means. First, an exceedingly sensitive instrumental method of detection is employed, which reveals the presence of very small amounts of dew, thus permitting temperature observation at a time when error is very small. Second, and

of greatest importance, each dew-point determination is derived graphically from a continuous series of observations which plot as two intersecting straight lines. Observations fixing one of these lines are made in absence of the liquid. In observations fixing the other straight line, quantity of dew (and hence temperature gradient error) decreases to zero at the intersection.

Thus there appears no reason to suspect that precision or accuracy of this apparatus should fall off materially upon application to samples of lower vapor content. As a matter of fact, precision at 90 per cent humidity was markedly superior to that at 100 per cent humidity.

### Application

It is indicated that fundamental obstacles to dew-point determination of high precision and accuracy, exclusive of instrumental and observational errors, are:

1. The inherent slowness of diffusional processes. This leads to hysteresis in determinations involving continuous temperature change. Methods involving control of amount of dew deposited and of heating rate might succeed in standardizing this hysteresis. Results would then show precision (sensitivity and reproducibility) but not absolute accuracy. Reduction of hysteresis, through slow heating, increases the time of a determination beyond that desirable.
2. With the elimination of hysteresis by adoption of the intermittent rise technic, there is indication of the presence of a double gaseous film adjacent to the liquid, of which the upper or unsaturated film is still present at temperatures above the dew point. This film appears to produce an effect, at least with regard to light transmission, similar in nature to a persistence of the dew itself. This effect affords explanation of the difficulty of obtaining concordant indications of dew point where reliance is placed upon visual observation.

The apparent way to obtain still sharper indications of dew point, and simultaneously to realize a shorter period of determination, is to cause the sample to move at high velocity across the surface on which dew is deposited. The object is to minimize film thicknesses, and also to increase diffusion rates. Correction for pressure changes would be necessary.

Such an application, in combination with photoelectric or other instrumental means of dew observation, would appear to be a useful research tool, as, for example, in the determination of pressure-phase relationships in complex hydrocarbon mixtures at constant temperature. Sensitive control of vapor mixtures in industrial processes presents another possibility.

The accuracy of dew-point determination which has been developed opens the way to possible new applications. For example, the measurement of very low concentrations of a vapor in a gas is rendered practicable by the combination of such accurate determination with the following suggested principle of operation: A reference mixture is first prepared, consisting of gas partially saturated with a selected vapor, and the dew point (with respect to that vapor) is determined. The sample, of unknown vapor concentration, is now pumped into the space occupied by the reference mixture, and the new dew point is determined. The difference in dew points is a sensitive measure of the added vapor concentration carried in by the unknown sample. Multiplied sensitivity could be attained by continuing to pump in the unknown sample until a total pressure of several atmospheres had been reached. In the latter case the effects of dissolved gas, and of increased pressure, upon the vapor pressure of the liquid phase should be considered.

### Summary and Conclusions

An apparatus has been designed which minimizes the known instrumental and observational errors in the determination of dew point.



The technic of applying this apparatus to the elucidation of the inherent difficulties of dew point determination has been developed.

Wide discrepancies are introduced by hysteresis in dew evaporation. These have been investigated and their extent has been indicated.

A technic for eliminating hysteresis, at the expense of time consumption, has been evolved.

It has been shown possible to obtain a precision of about  $\pm 0.01^\circ \text{C.}$  at 90 per cent humidity, and  $\pm 0.05^\circ \text{C.}$  at 100 per cent humidity. Observations on the saturated samples checked absolute values within the stated limits of precision (reproducibility).

A hypothesis has been advanced with regard to the structure of gaseous films adjacent to the liquid phase. From this hypothesis has been formulated a concept of the mechanism of dew formation and evaporation, which affords explanation of the difficulty in obtaining concordant dew point indications by visual means.

A means of increasing further the sharpness of dew indication, simultaneously decreasing the time required for a determination, has been outlined.

Application of accurate dew-point determination as a research tool has been considered.

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# Determination of Sugar in Curing Pickles and Dry-Curing Mixtures

## A Polarimetric Method

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ONE important phase of packing-house laboratory control over plant operations is the analysis of curing pickles both new and used, and dry-curing mixtures. The former are solutions of sodium chloride containing sucrose in the form of raw or granulated sugar and the regular curing ingredients, sodium nitrite and sodium nitrate, either singly or together. The concentration of sodium chloride varies from about 15 per cent to saturation, while the sugar range is from zero to about 5 per cent. Sodium nitrite and nitrate are present in considerably less amount, seldom exceeding 0.5 per cent for the nitrate and 0.2 per cent for the nitrite. Dry-curing mixtures differ from pickles in that they contain these ingredients in the dry state.

The sugar determination (by any of the recognized gravimetric or volumetric methods) consumes the most time and is the least accurate of the ingredient tests, and a quick and reasonably accurate method would greatly facilitate pickle and dry-cure control and save much time and labor in the laboratory.

### Use of Polariscope

The polariscope in the field of sugar chemistry is employed ordinarily on solutions containing sugars with no inorganic substances present. On account of its dependability and production of uniform results, particularly on sucrose, the instrument was considered suitable for this study, despite the corrections that necessarily would have to be applied with its use.

**CORRECTION FOR SODIUM CHLORIDE CONCENTRATION.** The literature contains numerous articles which demonstrate the depression of optical rotation of both sucrose and invert sugar towards the negative side in the presence of this salt. Unfortunately the data presented are scattered and entirely insufficient to develop the necessary curves for the methods desired. Moreover, few or no data are presented which show the effect of the higher concentrations of sodium chloride that are found in curing pickles. It was necessary, therefore, to develop the correction by several experiments.

**CORRECTION FOR INORGANIC IMPURITIES IN SODIUM CHLORIDE.** Ordinary curing salt contains these impurities (calcium sulfate, calcium chloride, magnesium chloride, etc.) in very small quantities, and the literature indicates that there is no great difference between their influence and the influence of sodium chloride upon the optical activity of sucrose. It was decided, because of this obviously negligible effect, not to consider them.

**CORRECTION FOR SODIUM NITRITE AND SODIUM NITRATE.** As only scattered data are available, it became necessary to develop this by experimentation.

**CORRECTION FOR PRESENCE OF INVERT SUGAR IN SUCROSE.** This factor possesses some significance. It would be possible to invert the solution containing the sucrose and calculate total sugar as invert, but this would add another step of considerable length. A study of numerous analyses of raw and granulated sugar disclosed that the invert content was fairly constant in both types. For all practical purposes an assumption could be made that there is 1.5 per cent of invert



sugar in the raw sugar, and 0.50 per cent in the granulated sugar. The errors due to the ordinary variations from these values are not appreciable. (For convenience, however, a formula giving the correction to apply to sugars having different invert values from these is presented later.)

TABLE I. SUCROSE DETERMINATIONS

Sucrose	Sodium Chloride	Sodium Nitrate	Sodium Nitrite	Reading ° V.	Sucrose Pounds per 100 gallons <sup>a,b</sup>	Added for correction <sup>c</sup> %
Pounds per 100 gallons						
15.00	...	..	..	+ 7.00	15.25	0.0
	50	..	..	+ 6.90	15.03	1.5
	100	..	..	+ 6.71	14.62	4.3
	150	..	..	+ 6.63	14.44	5.6
	200	..	..	+ 6.57	14.31	6.5
	250	..	..	+ 6.49	14.13	7.9
30.00	...	..	..	+13.77	29.99	0.0
	100	..	..	+13.37	29.12	3.0
	200	..	..	+13.07	28.47	5.3
	250	..	..	+12.87	28.03	7.0
	...	5.0	..	+13.78	30.01	0.0
	...	10.0	..	+13.85	30.17	0.0
	...	...	5.0	+13.74	29.93	0.0
	...	...	10.0	+13.79	30.03	0.0
40.00	...	..	..	+18.50	40.29	0.0
	50	..	..	+18.11	39.44	2.2
	100	..	..	+17.83	38.83	3.8
	150	..	..	+17.66	38.46	4.8
	200	..	..	+17.40	37.90	6.3
	225	..	..	+17.22	37.51	7.4
	256	..	..	+17.16	37.37	7.8
	...	2.5	..	+18.37	40.01	0.1
	...	...	1.0	+18.52	40.34	0.0

<sup>a</sup> Pounds per 100 U. S. gallons  $\times$  0.1198 = grams per 100 ml. Reading in ° V.  $\times$  2.1782 = pounds of sucrose per 100 gallons at 32° C. (3).  
<sup>b</sup> Calculated from the readings obtained.  
<sup>c</sup> The % corrections are based on the decrease obtained from zero salt. Thus, for 15 pounds of sucrose and 250 pounds of sodium chloride, the % to be added to the sucrose value already obtained (14.13 pounds) equals  $\frac{(15.25 - 14.13) \times 100}{14.13}$  or 7.9%.

CORRECTION FOR TEMPERATURE OF POLARIMETRIC READING and for volume of precipitate from the clarifying solution. The first is small for sucrose at room temperature but is pronounced for invert sugars. The volume of precipitate error is negligible and need not be considered.

Procedure

For new pickles—that is, fresh, as made up, containing no protein matter and only the invert sugar present in the original make-up sugar—and dry-curing mixtures, apply two correction factors: (1) a value for the invert sugar present in the sugar used in making the pickle, assuming a constant value for granulated and raw sugar, respectively, and (2) a factor for sodium chloride concentration and possibly one each for sodium nitrite and nitrate, the latter to be developed by experimentation. These two factors would be applied in order to the direct polarimetric reading on the clarified or unclarified pickle, or dry-curing mixture made up to volume. The temperature correction would be avoided by always reading at 25° C. or at some other constant level.

For used pickles (pickles removed from the tierce or box holding the meat during the process of curing and containing protein matter and a high proportion of invert sugar), the employment of polarimetric methods was inadvisable for several reasons: (1) A large factor must be used in the calculations, which limits accuracy; (2) the correction for sodium chloride is very large, also limiting accuracy; and (3) clarification of used pickles followed by inversion is an awkward operation. Consequently, extension of the work to used pickles was abandoned.

Sucrose

Pure, dried Difco sucrose was made up into a solution of known strength. Varying quantities of chemically pure sodium chloride were weighed into 100-ml. volumetric flasks,

and known amounts of the sucrose solution were then added to each. In a few cases, solutions containing sodium nitrite or sodium nitrate alone were prepared with sucrose. These were then made up to volume, mixed thoroughly, and polarized directly in a 200-mm. tube with white light filtered through a potassium dichromate cell, the solution being of such concentration that the percentage content of potassium dichromate multiplied by the length of the column in centimeters was equal to 9. The instrument employed in these tests was a J. and J. Fric, Bates-type saccharimeter, 200 mm. All readings were made at 32° C. The results are shown in Table I.

It follows from these data that there is a regular decrease in apparent values of sucrose with an increase in sodium chloride concentration. Another fact brought out is that sodium nitrite and sodium nitrate in the concentrations employed in pickle exert no appreciable effect on the rotation and consequently may be neglected as factors influencing the readings.

Table II presents the sucrose correction to be added to the uncorrected sucrose obtained from the polarimetric reading compensating for the presence of invert sugar.

TABLE II. INITIAL CORRECTION, FOR INVERT SUGAR

(Based on the assumption of 1.50% invert sugar and 98.50% sucrose in raw sugar and 0.50% invert sugar and 99.50% sucrose in granulated sugar. Add to sucrose from direct polarimetric reading, expressed in any unit of weight per volume at 20° C. such as grains per 100 ml. or pounds per 100 gallons. The correction will be in the same unit of weight per volume. Example: The correction for 10 pounds per 100 gallons at 25° C. is 0.21 pound per 100 gallons. For 10 grams per 100 ml. at 25° C. it is 0.21 gram per 10 ml.)

Sucrose Calculated from Polarimetric Reading <sup>a</sup>	Correction for Raw <sup>b</sup> Sugar	Correction for Granulated <sup>b</sup> Sugar	Sucrose Calculated from Polarimetric Reading <sup>a</sup>	Correction for Raw <sup>b</sup> Sugar	Correction for Granulated <sup>b</sup> Sugar
1	0.02	0.01	26	0.54	0.20
2	0.04	0.02	27	0.56	0.21
3	0.06	0.02	28	0.59	0.22
4	0.08	0.03	29	0.61	0.23
5	0.10	0.04	30	0.63	0.24
6	0.13	0.05	31	0.65	0.25
7	0.15	0.06	32	0.67	0.25
8	0.17	0.06	33	0.69	0.26
9	0.19	0.07	34	0.71	0.27
10	0.21	0.08	35	0.74	0.28
11	0.23	0.09	36	0.76	0.29
12	0.25	0.10	37	0.78	0.30
13	0.27	0.10	38	0.80	0.30
14	0.29	0.11	39	0.82	0.31
15	0.31	0.12	40	0.84	0.32
16	0.33	0.13	41	0.87	0.33
17	0.35	0.14	42	0.89	0.33
18	0.38	0.14	43	0.91	0.34
19	0.40	0.15	44	0.93	0.35
20	0.42	0.16	45	0.95	0.36
21	0.44	0.16	46	0.97	0.37
22	0.46	0.17	47	0.99	0.37
23	0.48	0.18	48	1.01	0.38
24	0.50	0.19	49	1.03	0.39
25	0.52	0.19	50	1.05	0.39

<sup>a</sup> In any unit of weight per volume at 25° C.  
<sup>b</sup> In same unit of weight per volume as sucrose in first column at 25° C

On the basis of the data developed, Table III was drawn up. It shows the sucrose correction to be added to the sucrose already corrected for invert sugar, as described above, for the presence of sodium chloride.

The methods outlined below utilize the facts which were brought out in the foregoing work. They are recommended for use in routine testing or for determinations where extreme accuracy is not required.

New Pickles

PICKLES MADE FROM RAW SUGAR. Fill a 100-ml. volumetric flask to the mark with pickle at a temperature of 25° C. Add 2 to 4 ml. (as necessary) of basic lead acetate and mix. (To prepare this reagent, boil 430 grams of neutral lead acetate, 130 grams of litharge, and 1 liter of distilled water for 30 minutes. Allow the mixture to cool and settle and then dilute the supernatant liquid to a specific gravity of 1.25 with recently boiled, distilled water.



TABLE III. FINAL CORRECTION, FOR SODIUM CHLORIDE CONCENTRATION

(Add to sucrose, expressed in any unit of weight per volume at 25° C., such as grams per 100 ml. or pounds per 100 gallons, corrected for invert sugar. The correction will be in the same unit of weight per volume. Example: The correction for 30 pounds of sucrose per 100 gallons at 25° C. for a sodium chloride concentration of 30 pounds per 100 gallons is 0.31 pound per 100 gallons. For 30 grams of sucrose per 100 ml. at 25° C. for a sodium chloride concentration of 30 grams per 100 ml. it is 0.31 gram per 100 ml.)

The table applies for values of sugar up to the equivalent of 50 pounds per 100 gallons as the experimental data went only that high. For example, if the units are expressed in grams per 100 ml., the table should not be used for sucrose values in excess of 6 grams per 100 ml.)

Sucrose Corrected for Invert <sup>a</sup> Sugar	Salt Concentration <sup>b</sup>																											
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200	210	220	230	240	250	260	265	
1	0.00	0.01	0.01	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.08	0.08	0.08
2	0.01	0.01	0.02	0.03	0.04	0.04	0.05	0.06	0.06	0.07	0.07	0.08	0.08	0.09	0.09	0.10	0.10	0.11	0.11	0.12	0.13	0.13	0.14	0.14	0.15	0.15	0.16	0.16
3	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15	0.15	0.16	0.17	0.18	0.19	0.20	0.20	0.21	0.22	0.23	0.24	0.24	0.24
4	0.01	0.03	0.04	0.06	0.07	0.08	0.10	0.11	0.12	0.14	0.15	0.16	0.17	0.18	0.20	0.20	0.22	0.23	0.24	0.25	0.26	0.27	0.28	0.29	0.30	0.32	0.32	
5	0.02	0.03	0.05	0.07	0.09	0.10	0.12	0.14	0.15	0.17	0.18	0.20	0.21	0.23	0.24	0.25	0.27	0.28	0.30	0.31	0.32	0.34	0.35	0.36	0.38	0.39	0.40	
6	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24	0.26	0.28	0.30	0.32	0.34	0.36	0.38	0.40	0.42	0.44	0.46	0.48	0.50	0.52	0.53	
7	0.02	0.05	0.07	0.10	0.13	0.15	0.17	0.20	0.22	0.24	0.26	0.28	0.30	0.32	0.35	0.35	0.38	0.40	0.42	0.44	0.46	0.48	0.50	0.52	0.54	0.56	0.57	
8	0.03	0.06	0.08	0.12	0.14	0.16	0.20	0.22	0.24	0.28	0.30	0.32	0.34	0.36	0.40	0.40	0.44	0.46	0.48	0.50	0.53	0.54	0.56	0.58	0.60	0.64	0.64	
9	0.03	0.06	0.09	0.13	0.16	0.19	0.22	0.25	0.28	0.31	0.33	0.36	0.39	0.41	0.44	0.46	0.49	0.51	0.54	0.57	0.59	0.61	0.64	0.66	0.68	0.71	0.73	
10	0.03	0.07	0.10	0.14	0.18	0.21	0.24	0.28	0.31	0.34	0.37	0.40	0.43	0.46	0.49	0.51	0.54	0.57	0.60	0.63	0.65	0.68	0.71	0.73	0.76	0.79	0.81	
11	0.04	0.08	0.12	0.15	0.20	0.23	0.26	0.31	0.34	0.37	0.41	0.44	0.47	0.51	0.54	0.56	0.59	0.63	0.66	0.69	0.72	0.75	0.78	0.80	0.84	0.87	0.89	
12	0.04	0.08	0.13	0.17	0.22	0.25	0.29	0.34	0.37	0.41	0.44	0.48	0.52	0.55	0.59	0.61	0.65	0.68	0.72	0.76	0.78	0.82	0.85	0.88	0.91	0.95	0.97	
13	0.05	0.09	0.14	0.18	0.23	0.27	0.31	0.36	0.40	0.44	0.48	0.52	0.56	0.60	0.64	0.66	0.70	0.74	0.78	0.82	0.85	0.88	0.92	0.95	0.99	1.03	1.05	
14	0.05	0.10	0.15	0.20	0.25	0.29	0.34	0.39	0.43	0.48	0.52	0.56	0.60	0.64	0.69	0.72	0.76	0.80	0.84	0.88	0.91	0.95	0.99	1.02	1.06	1.11	1.13	
15	0.05	0.10	0.16	0.21	0.27	0.31	0.36	0.42	0.46	0.51	0.55	0.60	0.64	0.69	0.74	0.77	0.81	0.85	0.90	0.94	0.98	1.02	1.07	1.10	1.14	1.19	1.22	
16	0.06	0.11	0.17	0.22	0.29	0.34	0.38	0.45	0.50	0.54	0.59	0.64	0.69	0.74	0.79	0.82	0.86	0.91	0.96	1.01	1.04	1.09	1.14	1.17	1.22	1.26	1.30	
17	0.06	0.12	0.18	0.24	0.31	0.36	0.41	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.83	0.87	0.92	0.97	1.02	1.07	1.11	1.16	1.21	1.24	1.29	1.34	1.38	
18	0.06	0.13	0.19	0.25	0.32	0.38	0.43	0.50	0.56	0.61	0.67	0.72	0.77	0.83	0.88	0.92	0.97	1.03	1.08	1.13	1.17	1.23	1.28	1.32	1.37	1.42	1.46	
19	0.07	0.13	0.20	0.27	0.34	0.40	0.46	0.53	0.59	0.65	0.70	0.76	0.82	0.87	0.93	0.97	1.03	1.09	1.14	1.20	1.24	1.29	1.35	1.39	1.44	1.50	1.54	
20	0.07	0.14	0.21	0.28	0.36	0.42	0.48	0.56	0.62	0.68	0.74	0.80	0.86	0.92	0.98	1.02	1.08	1.14	1.20	1.26	1.30	1.36	1.42	1.46	1.52	1.58	1.62	
21	0.07	0.15	0.22	0.29	0.38	0.44	0.50	0.59	0.65	0.71	0.78	0.84	0.90	0.97	1.03	1.07	1.14	1.20	1.26	1.33	1.37	1.43	1.49	1.53	1.60	1.66	1.70	
22	0.08	0.15	0.23	0.31	0.40	0.46	0.53	0.62	0.68	0.75	0.81	0.88	0.94	1.01	1.08	1.12	1.19	1.25	1.32	1.39	1.43	1.50	1.56	1.61	1.67	1.74	1.78	
23	0.08	0.16	0.24	0.32	0.41	0.48	0.55	0.64	0.71	0.78	0.85	0.92	0.99	1.06	1.13	1.17	1.24	1.31	1.38	1.45	1.50	1.57	1.63	1.68	1.75	1.82	1.86	
24	0.08	0.17	0.25	0.34	0.43	0.50	0.58	0.67	0.74	0.82	0.89	0.96	1.03	1.10	1.18	1.22	1.30	1.37	1.44	1.51	1.56	1.63	1.71	1.75	1.82	1.90	1.94	
25	0.09	0.17	0.26	0.35	0.45	0.52	0.60	0.70	0.78	0.85	0.92	1.00	1.07	1.15	1.23	1.27	1.35	1.43	1.50	1.58	1.63	1.70	1.78	1.83	1.90	1.98	2.02	
26	0.09	0.18	0.27	0.36	0.47	0.55	0.62	0.73	0.81	0.88	0.96	1.04	1.12	1.20	1.27	1.33	1.41	1.48	1.56	1.64	1.69	1.77	1.85	1.90	1.98	2.05	2.11	
27	0.09	0.19	0.28	0.38	0.49	0.57	0.65	0.76	0.84	0.92	1.00	1.08	1.16	1.24	1.32	1.38	1.46	1.54	1.62	1.70	1.76	1.83	1.92	1.97	2.05	2.14	2.19	
28	0.10	0.20	0.29	0.39	0.50	0.59	0.67	0.78	0.87	0.95	1.04	1.12	1.20	1.29	1.37	1.43	1.51	1.60	1.68	1.77	1.82	1.90	1.99	2.05	2.13	2.21	2.27	
29	0.10	0.20	0.30	0.41	0.52	0.61	0.70	0.81	0.90	0.99	1.07	1.16	1.25	1.33	1.42	1.48	1.57	1.65	1.74	1.83	1.89	1.98	2.06	2.12	2.21	2.29	2.35	
30	0.10	0.21	0.31	0.42	0.54	0.63	0.72	0.84	0.93	1.02	1.11	1.20	1.29	1.38	1.47	1.53	1.62	1.71	1.80	1.89	1.95	2.04	2.13	2.19	2.28	2.37	2.43	
31	0.11	0.22	0.32	0.43	0.56	0.65	0.74	0.87	0.96	1.05	1.15	1.24	1.33	1.43	1.52	1.58	1.67	1.77	1.86	1.95	2.02	2.11	2.20	2.27	2.36	2.45	2.51	
32	0.11	0.22	0.34	0.45	0.58	0.67	0.77	0.90	0.99	1.09	1.18	1.28	1.38	1.47	1.57	1.63	1.73	1.83	1.92	2.02	2.08	2.18	2.27	2.34	2.43	2.53	2.59	
33	0.12	0.23	0.35	0.46	0.59	0.69	0.79	0.93	1.02	1.12	1.22	1.32	1.42	1.52	1.62	1.68	1.78	1.88	1.98	2.08	2.15	2.24	2.33	2.41	2.51	2.61	2.68	
34	0.12	0.24	0.36	0.48	0.61	0.71	0.84	0.98	1.09	1.19	1.30	1.40	1.50	1.61	1.72	1.78	1.84	1.94	2.04	2.14	2.21	2.31	2.42	2.48	2.58	2.69	2.76	
35	0.12	0.25	0.37	0.49	0.63	0.74	0.88	1.01	1.12	1.23	1.33	1.44	1.55	1.66	1.77	1.83	1.95	2.05	2.16	2.27	2.34	2.45	2.56	2.63	2.74	2.84	2.92	
36	0.13	0.25	0.38	0.50	0.65	0.76	0.86	1.01	1.12	1.23	1.33	1.44	1.55	1.66	1.77	1.89	1.95	2.05	2.16	2.28	2.34	2.45	2.56	2.63	2.70	2.81	2.93	
37	0.13	0.26	0.39	0.52	0.67	0.78	0.89	1.04	1.15	1.26	1.37	1.48	1.59	1.70	1.81	1.89	2.00	2.11	2.22	2.33	2.41	2.52	2.63	2.70	2.81	2.93	3.00	
38	0.13	0.27	0.40	0.53	0.68	0.80	0.91	1.07	1.18	1.29	1.41	1.52	1.63	1.75	1.86	1.93	2.05	2.17	2.28	2.40	2.47	2.58	2.70	2.77	2.89	3.00	3.08	
39	0.14	0.27	0.41	0.55	0.70	0.82	0.94	1.09	1.21	1.33	1.44	1.56	1.68	1.80	1.91	1.99	2.11	2.22	2.34	2.46	2.54	2.65	2.77	2.85	2.96	3.08	3.16	
40	0.14	0.28	0.42	0.56	0.72	0.84	0.96	1.12	1.24	1.36																		



Solid basic lead acetate may be substituted for the normal salt and litharge in the preparation of the solution, 1.) Filter through a dry filter paper and reject the first 10 ml. Polarize the filtrate in a 200-mm. tube, using sodium light or its equivalent.

CALCULATIONS. Sucrose (in pounds per 100 gallons at 25° C.) = reading × 2.1735 or, sucrose (in grams per 100 ml. at 25° C.) = reading × 0.2604.

If the result is expressed in pounds per 100 gallons, apply Table II under "raw sugar" for invert sugar and add the correction to the sucrose obtained above.

Apply Table III for the sodium chloride concentration, adding the correction to the sucrose corrected for invert sugar.

Correct for the dilution by the clarifying reagent, which gives the correct total sugar expressed as sucrose in pounds per 100 gallons at the temperature of the reading (or in grams per 100 ml., depending upon the method of calculation that has been employed).

To calculate to pounds per 100 gallons or grams per 100 ml. at another temperature, multiply the result by  $S_2/S_1$  where

$$S_2 = \text{specific gravity (at temperature desired, } ^\circ \text{C.)}$$
$$\text{and } S_1 = \text{specific gravity (25} ^\circ \text{C.)}$$

$$\frac{(4^\circ \text{C.})}{(4^\circ \text{C.})}$$

PICKLES MADE FROM GRANULATED SUGAR. Polarize the sample direct without clarification. The corrections and calculations are the same as for raw-sugar pickles, except that the corrections under "granulated sugar" in Table II should be used, and there is no adjustment for dilution by the clarifying agent.

In case a sugar is employed known to contain invert sugar in significantly different amount than the values assumed here (1.5 per cent for raw sugar and 0.5 per cent for granulated sugar) the following formula may be used to obtain the correct factor to add.

If results are expressed as pounds per 100 gallons:

$$\frac{\text{Pounds of sucrose per 100 gallons at 25}^\circ \text{C. (uncorrected)} \times 100}{\text{Reading when 25 grams of sugar are made to 100 ml. at 25}^\circ \text{C.}^1}$$

$$- \frac{\text{pounds of sucrose per 100 gallons at 25}^\circ \text{C. (uncorrected)}}{1}$$

If results are expressed as grams per 100 ml.:

$$\frac{\text{Grams of sucrose per 100 ml. at 25}^\circ \text{C. (uncorrected)} \times 100}{\text{Reading when 25 grams of sugar are made to 100 ml. at 25}^\circ \text{C.}^1}$$

$$- \frac{\text{grams of sucrose per 100 ml. at 25}^\circ \text{C. (uncorrected)}}{1}$$

$$^1 \text{ Equals: } \frac{(\% \text{ of sucrose} \times 99.85)}{100} + \frac{(\% \text{ of invert sugar} \times -27.50)}{100}$$

(26 grams of sucrose will read 99.85° V. at 25° C., the value dropping 0.03° for each ° C. above 20° C., 2.)

Dry-Curing Mixtures

A solution of satisfactory sugar concentration is prepared from the sample and polarized directly in a 200-mm. tube at 25° C., when granulated sugar is used.

CALCULATION. Sucrose (in pounds per 100 gallons at 25° C. = reading × 2.1735 or, sucrose (in grams per 100 ml. at 25° C.) = reading × 0.2604.

Apply Table II under "granulated sugar" for the invert sugar correction, adding it to the sucrose obtained above.

Apply Table III for the sodium chloride concentration correction (the concentration of sodium chloride in the solution of dry-curing mixture must be determined in pounds per 100 gallons) and add this to the sucrose corrected for invert sugar.

Then the percentage of total sugar as sucrose equals:

$$\frac{\text{Corrected total sugar (in pounds per 100 gallons at 25}^\circ \text{C.)} \times \text{volume of solution prepared (in ml.)}}{8.344 \times \text{weight of dry-curing mixture made to volume (in grams)}}$$

or

$$\frac{\text{Corrected total sugar (in grams per 100 ml. at 25}^\circ \text{C.)} \times \text{volume of solution prepared (in ml.)}}{\text{Weight of dry-curing mixture made to volume (in grams)}}$$

If raw sugar is used, the same procedure applies, except that a clarifying agent is employed with subsequent filtration. Add the clarifying agent to the flask before making up to volume, thus avoiding the correction for dilution which is necessary with pickles. In the calculations, apply the raw sugar correction for invert sugar.

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The Effect of Phosphate on the Determination of Tungsten

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IT HAS long been recognized that phosphates interfere with the quantitative determination of tungsten, yet very little work has been conducted to determine the cause and the extent of that interference. It has generally been conceived as due to the formation of a phosphotungstic acid complex; the extent of that interference is virtually unknown. Hutchin (1, 3) concluded that phosphates do not interfere with the determination of tungsten by the cinchonine method; but Hillebrand and Lundell (2) give four analyses, the results of which would indicate that phosphates cause low results in the determination of tungsten by the acid precipitation method and high results when the cinchonine method is used. Aside from these five analyses, no other relevant quantitative data were found in the literature.

The present work was therefore undertaken in order to ascertain the extent, and, if possible, the cause of the interfer-

ence of phosphate in the quantitative determination of tungsten by the acid precipitation and by the cinchonine precipitation procedures. The method of attack consisted essentially of adding increments of phosphate solution to a fixed amount of a sodium tungstate solution and determining the tungsten trioxide by the two methods, standard procedures being followed.

Preparation and Standardization of Solutions

SODIUM TUNGSTATE. A solution of this salt was prepared containing approximately 0.1000 gram of WO<sub>3</sub> per 40 ml., and was standardized by the cinchonine method (5) and by the benzidine method of von Knorre (4).

DISODIUM HYDROGEN PHOSPHATE. A stock solution of this salt was prepared which contained 0.2980 gram of P<sub>2</sub>O<sub>5</sub> per 40.00 ml. Its concentration was determined by precipitation of



$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , ignition to  $\text{Mg}_2\text{P}_2\text{O}_7$ , and calculation of the results to  $\text{P}_2\text{O}_5$ . The solution was diluted for use.

**CINCHONINE REAGENT.** Fifty grams of cinchonine were dissolved in 400 ml. of 6 *N* hydrochloric acid and the solution was filtered before use.

### Acid Precipitation Procedure

To 40.00 ml. of the standardized tungstate solution contained in a 250-ml. beaker a definite amount of the phosphate solution was added. The solution was brought nearly to boiling on a hot plate, and 40 ml. of concentrated hydrochloric acid and 15 ml. of concentrated nitric acid were added. The solution was boiled down to a volume of 50 ml., 5 ml. of concentrated nitric acid were added, and the solution was further evaporated to a volume of 10 ml. It was then made up to 150 ml. with hot water, allowed to simmer for half an hour, and left to stand in the cold overnight.

The precipitated tungsten trioxide was filtered with the aid of filter pulp (made by digesting ashless filter paper with concentrated hydrochloric acid and diluting with water), washed with dilute hydrochloric acid (1 to 19), dried, and ignited at  $800^\circ \pm 10^\circ \text{C}$ . in an electric muffle furnace to constant weight. Determinations were made in triplicate.

TABLE I. EFFECT OF PHOSPHATE ON PRECIPITATION OF TUNGSTEN BY ACID

(WO <sub>3</sub> present in all solutions, 0.1003 gram)					
P <sub>2</sub> O <sub>5</sub>	WO <sub>3</sub> Precipitated				By HClO <sub>4</sub>
	By HCl-HNO <sub>3</sub>				
Mg.	Gram	Gram	Gram	Av. Gram	Gram
0.37	0.0948	0.0947	0.0936	0.0944	0.0891
0.75	0.0902	0.0900	0.0904	0.0902	0.0769
1.45	0.0822	0.0818	0.0837	0.0826	0.0605
2.24	0.0743	0.0743	0.0772	0.0752	0.0356
2.98	0.0687	0.0689	0.0700	0.0692	0.0244
4.47	0.0568	0.0584	0.0592	0.0581	0.0202
5.96	0.0523	0.0528	0.0512	0.0523	0.0173
7.45	0.0476	0.0479	0.0459	0.0472	0.0150
8.94	0.0409	0.0440	0.0469	0.0439	....
10.4	0.0333	0.0363	0.0364	0.0354	....
11.9	0.0332	0.0334	0.0367	0.0344	....
13.4	0.0295	0.0309	0.0347	0.0317	....
14.9	0.0307	0.0360	0.0268	0.0312	....
16.4	0.0413	0.0322	0.0129	0.0288	....
17.9	0.0211	0.0374	0.0151	0.0245	....

Because of the recent widespread use of perchloric acid as an oxidizing acid of low volatility, and more particularly because of certain discrepancies which arose in the use of the hydrochloric-nitric acid procedure with the higher amounts of added phosphate, it was decided to try the effect of 15 ml. of perchloric acid in place of the hydrochloric-nitric acid mixture. One determination using the perchloric acid modification was carried out along with the triplicates by the hydrochloric-nitric acid method. Results are recorded in Table I and plotted in Figure 1.

In the absence of phosphate, the use of perchloric acid in place of the usual hydrochloric-nitric acid mixture in the acid precipitation method results in complete precipitation of the tungsten, as is shown by Table II, which represents a typical standardization of tungstate solution.

TABLE II. EFFECTIVENESS OF PERCHLORIC ACID IN TUNGSTATE STANDARDIZATION

(WO <sub>3</sub> present in all solutions, 0.1003 gram)			
Cinchonine method	WO <sub>3</sub> Precipitated—		HClO <sub>4</sub> method
	Benzidine method		
Gram	Gram	Gram	Gram
0.1005	0.1001		0.1002
0.1003	0.1001		0.1002
0.1002	0.1000		0.1004
0.1005	0.1002		....
Av. 0.1004	0.1001		0.1003

The use of perchloric acid in the standardization procedure obviates the annoying characteristic of the tungsten trioxide precipitate to cling tenaciously to the sides of the beaker, a tendency which is so noticeable in the hydrochloric-nitric acid treatment. The possibility of the solutions evaporating to complete dryness and baking is practically eliminated, and the tungsten trioxide is precipitated in a form which is easily

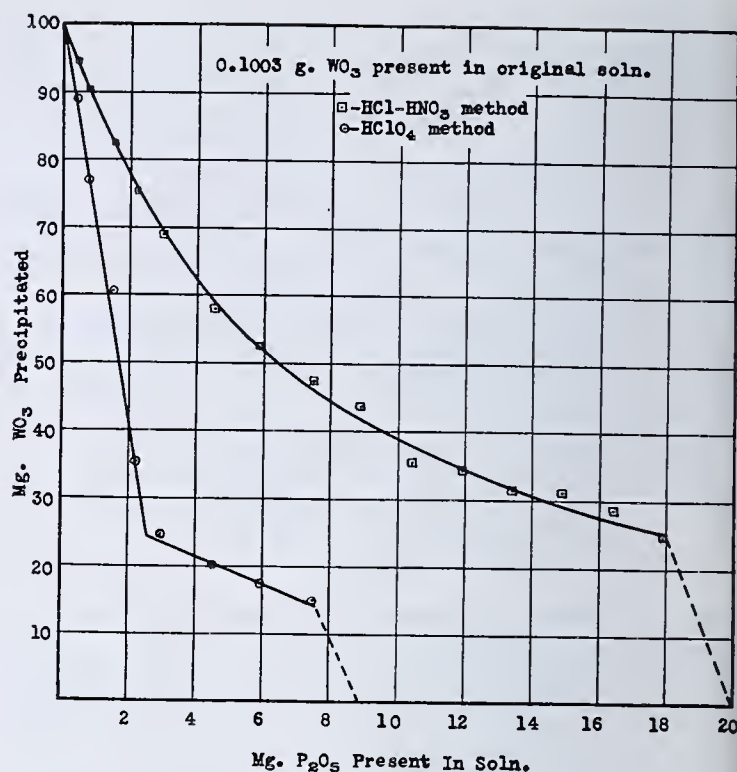


FIGURE 1. EFFECT OF PHOSPHATE ON DETERMINATION OF TUNGSTEN BY ACID PRECIPITATION METHOD

filtered. The use of perchloric acid in place of the hydrochloric-nitric acid mixture is therefore highly recommended.

### Cinchonine Method

The cinchonine method was similar to the acid precipitation procedure, but with the addition of 10 ml. of cinchonine reagent after the dilution to 150 ml. The precipitate upon the filter was washed with a hot cinchonine wash solution prepared by diluting 30 ml. of cinchonine reagent and 30 ml. of concentrated hydrochloric acid to 1 liter with water. In the cinchonine method, increasing amounts of phosphate solution caused decreasing amounts of tungsten trioxide to be precipitated by the acid digestion treatment, but the addition of the cinchonine produced a copious white precipitate, later found to be cinchonine phosphotungstate. Solutions containing phosphate equivalent to 20 mg. or more of  $\text{P}_2\text{O}_5$  formed no tungsten trioxide precipitate by the acid digestion treatment, but the addition of cinchonine produced copious precipitation. In view of this fact, the acid digestion procedure was omitted with solutions containing more than 20 mg. of phosphorus pentoxide. (Where the acid digestion was omitted, 3.5 ml. of concentrated nitric acid were added to the original solution, which, with the 60 milliequivalents of  $\text{H}^+$  included with the cinchonine reagent, then contained 118 milliequivalents of  $\text{H}^+$ . This acidity was previously determined to be present in the final filtrate of solutions carried out by the acid precipitation method. It was thought best to make the acidity the same in the two methods.)

The results of determinations by this method appear in Table III.

Because of the consistency of the high results obtained with 20 mg. or more of phosphorus pentoxide, it was felt that there was being precipitated a cinchonine phosphotungstate, which on ignition yielded one of the phosphotungstic anhydrides. On the assumption that the ignited residue contained all the original tungsten trioxide, and that the excess in weight was due to phosphorus pentoxide, the composition of the residue was calculated to correspond to that of the anhydride of one of the well-known phosphotungstic acids,  $\text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot n\text{H}_2\text{O}$ .

Further evidence of the truth of this assumption was obtained by precipitating the tungsten trioxide by the cinchonine procedure from a solution containing one and one-half times the amount of tungsten trioxide previously used, together with a sufficient quantity of phosphorus pentoxide. Thus, with 0.1497 gram of tungsten trioxide present in the



original solution, together with 0.0569 gram of phosphorus pentoxide, the average of three determinations gave  $0.1535 \pm 0.0002$  gram of residue. This checks with the theoretical yield of 0.1535 gram calculated on the assumption that the composition of the residue is  $P_2O_5 \cdot 24WO_3$ .

TABLE III. EFFECT OF PHOSPHATE ON PRECIPITATION OF TUNGSTEN BY CINCHONINE

( $WO_3$  present in all solutions, 0.0998 gram)

$P_2O_5$ Mg.	Weight of Residue			Av. Gram
	Gram	Gram	Gram	
3.0	0.1003	0.1007	0.1005	0.1005
6.0	0.1008	0.1011	0.1011	0.1010
10.0	0.1014	0.1015	0.1015	0.1015
15.0	0.1017	0.1015	0.1016	0.1016
20.0	0.1024	0.1023	0.1025	0.1024
37.3	0.1023	0.1024	0.1022	0.1023
55.9	0.1016	0.1025	0.1023	0.1021
74.5	0.1020	0.1020	0.1023	0.1021
93.1	0.1019	0.1023	0.1025	0.1024
120.0	0.1016	0.1020	0.1023	0.1020
149.0	0.1018	0.1019	0.1036	0.1024
447.0	0.1025	0.1028	0.1030	0.1027

To prove further the composition of the residue, analyses for phosphorus pentoxide and for tungsten trioxide were carried out on samples prepared from the ignited residues of the precipitates obtained by the cinchonine precipitation from solutions containing 0.6 gram of  $WO_3$  and 0.3 gram of  $P_2O_5$ . A number of such precipitations and ignitions yielded a combined residue of 4.46 grams.

The phosphorus pentoxide was determined by fusion of portions of the residue with anhydrous sodium carbonate in a nickel crucible, leaching with acidified water, boiling, precipitating with magnesia mixture in the presence of tartaric acid, and subsequent ignition to  $Mg_2P_2O_7$ . The results are given in Table IV.

TABLE IV. ANALYSIS OF RESIDUE FOR  $P_2O_5$

Weight of Sample Gram	Weight of $Mg_2P_2O_7$ Gram	Weight of $P_2O_5$	
		Observed Gram	Calcd. for $P_2O_5 \cdot 24WO_3$ Gram
0.4930	0.0194	0.0124	0.0123
0.5211	0.0197	0.0126	0.0130
0.5095	0.0199	0.0127	0.0127
0.5171	0.0200	0.0128	0.0129
		Av. 0.0126	0.0127

Two further samples were taken and both the phosphorus pentoxide content and the tungsten trioxide content were determined. Each sample was fused and the phosphorus pentoxide determined as before. The filtrate from the phosphorus pentoxide determination was diluted to 500 ml. in a volumetric flask and tungsten was determined in a 100-ml. aliquot by the benzidine method of von Knorre (4). The results are given in Table V.

TABLE V. ANALYSIS OF RESIDUE

Weight of Sample Gram	Weight of $Mg_2P_2O_7$ Gram	Weight of $P_2O_5$		Weight of $WO_3$	
		Observed Gram	Calcd. for $P_2O_5 \cdot 24WO_3$ Gram	Observed Gram	Calcd. for $P_2O_5 \cdot 24WO_3$ Gram
0.5543	0.0214	0.0137	0.0138	.....	.....
0.1109	.....	.....	.....	0.1078	0.1081
0.5778	0.0227	0.0145	0.0144	.....	.....
0.1156	.....	.....	.....	0.1125	0.1127

TABLE VI. COMPOSITION OF RESIDUE

(0.0998 gram of  $WO_3$  present in original solutions)

$P_2O_5$ Mg.	$WO_3$ Pptd. Gram	$WO_3$ in Soln. Gram	$P_2O_5 \cdot 24WO_3$ Equivalent to $WO_3$ in Soln. Gram	Weight of Residue Calcd. as $P_2O_5 \cdot 24WO_3$ Gram	Actual Weight of Residue Gram
3.0	0.0692	0.0306	0.0314	0.1006	0.1005
6.0	0.0523	0.0475	0.0487	0.1010	0.1010
10.0	0.0377	0.0621	0.0636	0.1013	0.1015
15.0	0.0312	0.0686	0.0703	0.1015	0.1016

The composition of the residue having been ascertained, attention was directed to the results obtained in the cinchonine procedure, where relatively small amounts of phosphate ( $< 20$  mg. of  $P_2O_5$ ) were present. In this range, experiment showed some precipitation of tungsten trioxide by the acid digestion procedure, followed by the formation of an additional precipitate by cinchonine. It was felt that the residues obtained were a mixture of  $WO_3$  and  $P_2O_5 \cdot 24WO_3$ . To show this, the amounts of tungsten trioxide present in a series of ignited precipitates were determined from Table I. The tungsten trioxide held in solution was then assumed to be precipitated as the phosphotungstate by the addition of the cinchonine, and the corresponding weight of  $P_2O_5 \cdot 24WO_3$  was then calculated. The results are shown in Table VI.

The close agreement of the actual and calculated values for weights of the residues indicates the validity of the assumption of the composition of the residue in the range of phosphate concentration employed.

## Discussion

Examination of the results obtained by the acid precipitation method yields two facts, one of practical importance, the other of theoretical interest. It is evident, in the first place, from both Table I and Figure 1, that the acid precipitation method for the determination of tungsten leads to low results in the presence of even small amounts of phosphate, and that the error increases with increasing amounts of phosphate. The second point of interest lies in the failure to obtain check results with solutions containing relatively large amounts of phosphate. This was attributed to the probable formation of some paratungstate in the highly acidified, hot phosphate-tungstate solution, the paratungstate not being decomposed by acids as are normal tungstates. The presence of the phosphate retards the tungsten trioxide precipitation and, therefore, allows time for paratungstate formation.

In the cinchonine method, any amount of phosphate causes high results. Increasing amounts of phosphate up to about 20 mg. of  $P_2O_5$  per 100 mg. of  $WO_3$  give increasing weights of residue, because of the precipitation of a decreasing amount of tungsten trioxide and a correspondingly increasing amount of the cinchonine phosphotungstate. Amounts of phosphate greater than 20 mg. of  $P_2O_5$  per 100 mg. of  $WO_3$  give uniform but high results because of the precipitation of only cinchonine phosphotungstate, the ignition of which yields  $P_2O_5 \cdot 24WO_3$ .

## Summary

The acid precipitation method for the determination of tungsten is unreliable in the presence of even small amounts of phosphate.

An explanation for the erratic results obtained in a series of triplicate determinations has been attributed to the formation of paratungstate under the experimental conditions.

Increasing amounts of phosphate up to about 20 mg. of  $P_2O_5$  per 100 mg. of  $WO_3$  give increasingly higher results in the determination of tungsten by the cinchonine method.

Amounts of phosphate greater than about 20 mg. of  $P_2O_5$  per 100 mg. of  $WO_3$  cause uniform but high results in the cinchonine procedure. This has been shown to be due to the precipitation of a cinchonine phosphotungstate, the ignition of which leaves a residue of the formula  $P_2O_5 \cdot 24WO_3$ .

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# Determination of Total Reducing Sugars and of Dextrose and Levulose in Cane Molasses

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THE work previously reported on the determination of dextrose and levulose in raw sugars (9, 10) has been extended to the analysis of cane molasses, the same principles being applied. However, the Munson and Walker method was selected for the determination of the total reducing sugars, in place of the Lane and Eynon method, because the former method is used almost exclusively in this country for trade analyses of molasses, is the official method of the U. S. Treasury Department, and has been adopted tentatively also by the International Commission for Uniform Methods of Sugar Analysis (4). The present Munson and Walker tables give only invert sugar in the presence of sucrose, and it was therefore necessary first to establish a table for dextrose and for levulose, separately, in the presence of sucrose, at a total sugar concentration of 0.4 gram in 50 ml. of solution. The pure dextrose and levulose used for this purpose were obtained from the National Bureau of Standards, the moisture being first removed by careful drying at low temperature *in vacuo*.

Twenty different weights of dextrose and of levulose, ranging from 20 to 228 mg., plus the required amount of pure sucrose, were used for the fundamental data, and also thirteen different weights of mixtures of equal parts of dextrose and levulose, plus sucrose, in order to compare the results with those obtained by Munson and Walker with invert sugar prepared from sucrose. The copper was weighed as cupric oxide, a method which is recognized as one of the most accurate when no impurities are present besides the sugars (1).

The method of least squares, applied to the fundamental data by Louis Sattler, of this laboratory, gave the following equations, where  $D$ ,  $L$ ,  $I$ , and  $CuO$  signify milligrams of dextrose, levulose, invert sugar, and cupric oxide, respectively:

$$\begin{aligned} D &= 0.38476 CuO + 0.00009436 CuO^2 - 3.177 \\ L &= 0.4305 CuO + 0.0000611 CuO^2 - 3.412 \\ I &= 0.40016 CuO + 0.00009631 CuO^2 - 2.9911 \end{aligned}$$

The milligrams of invert sugar corresponding to given quantities of cupric oxide were found to be slightly different from those given by Munson and Walker, as may be noted from Table I.

TABLE I. DETERMINATION OF INVERT SUGAR

CuO Mg.	Invert Sugar	
	M. and W. Mg.	E. and Z. Mg.
50	17.5	17.3
100	38.1	38.0
150	59.2	59.2
200	80.7	80.9
250	102.7	103.1
300	125.0	125.7
350	147.9	148.9
400	171.4	172.5
450	195.5	196.6
500	220.1	221.2

Below 150 mg. of cupric oxide the invert sugar figures of the writers are a little lower than those of Munson and Walker, but above that point the values found by the writers become increasingly larger than those given by Munson and Walker. The complete table (Table V) based on the experiments of the writers has been arranged in a

form somewhat different from that usually employed, to facilitate its use for the particular purpose in hand.

The method of Jackson and Mathews (5) was used, as heretofore, to determine the apparent levulose. In order to find dextrose,  $D$ , and levulose,  $L$ , the total reducing sugars,  $R_1$ , and the apparent levulose,  $R_2$ , are expressed as mg. of levulose, and the following formulas are used for the calculation:

$$\begin{aligned} aD + L &= R_1 \\ 0.081D + L &= R_2 \end{aligned}$$

where  $a$  is the variable reducing ratio of dextrose to levulose for the Munson and Walker method, found from Table V for all possible proportions between dextrose and levulose; and 0.081 is the constant reducing ratio of dextrose to levulose in the method of Jackson and Mathews.

Solving for  $D$  and  $L$ :

$$D = \frac{R_1 - R_2}{a - 0.081}$$

$$L = R_1 - aD$$

The results are calculated by a series of approximations. In the first calculation the value of  $a$  is taken from the column for invert sugar (50  $D$ , 50  $L$ ) in Table V. If the result shows a different ratio of dextrose to levulose, a second calculation is made with the value of  $a$  corresponding to that ratio. A third approximation is usually unnecessary.

TABLE II. CHECK ANALYSES WITH KNOWN MIXTURES OF DEXTROSE, LEVULOSE, AND SUCROSE

No.	Sucrose Taken Mg.	Dextrose Taken Mg.	Dextrose Found Mg.	Levulose Taken Mg.	Levulose Found Mg.
1	320.0	56.0	56.3	24.0	23.5
2	320.0	32.0	30.6	48.0	48.4
3	280.0	84.0	83.0	36.0	36.2
4	280.0	48.0	47.4	72.0	71.5
5	240.0	112.0	113.9	48.0	48.3
6	240.0	64.0	61.4	96.0	97.1
7	200.0	140.0	137.3	60.0	60.8
8	320.0	40.0	41.0	40.0	38.4
9	240.0	80.0	80.3	80.0	79.9
10	200.0	100.0	102.1	100.0	98.7
Av.	...	75.6	75.3	60.4	60.3

This method was tested by analyzing a number of sugar mixtures containing known proportions of dextrose, levulose, and sucrose. In these analyses the copper was not determined gravimetrically, however, because the method is to be used for the analysis of low-purity products like molasses, in which case the copper precipitate is always contaminated with organic and mineral impurities, and consequently too high results are apt to be obtained by weighing in the form of cupric oxide. Although the organic impurities can be removed by ignition to cupric oxide, the mineral matter cannot. Reduction of the cupric oxide to metallic copper, by means of hydrogen or alcohol vapors, as described in the U. S. Treasury method, does not obviate this difficulty, because the mineral impurities still remain with the copper. This has been shown by Meade (6) who reports that the copper calculated from the cupric oxide usually checks with the copper reduced by alcohol vapor within a fraction of a milligram, which is well within the permissible difference between duplicate determinations as



either oxide or metal. This observation has been fully confirmed in this laboratory.

For the reasons indicated it was decided to determine the copper in the precipitate by a volumetric method, and the widely used ferric sulfate-permanganate method was chosen for this purpose. The voluminous literature on this subject will not be reviewed in detail, but attention is called to the work of Schoorl and Regenbogen (8) and of Bruhns (3). These authors found that the low results usually obtained with the permanganate method are caused by reoxidation of the ferrous sulfate when the cuprous oxide is dissolved in a mixture of ferric sulfate and sulfuric acid. If, however, the cuprous oxide is first dissolved in ferric sulfate or ferric alum solution, and the sulfuric acid not added until immediately before the titration with permanganate, correct results are obtained. The writers have therefore adopted the method as modified by Pick (7). The end point of the permanganate titration can be fixed more sharply by the use of phenanthroline indicator. The ferric sulfate-permanganate method in the modified form has given very satisfactory results in this laboratory.

The results of the check analyses made by the combined method as described are shown in Table II.

Considering that the method is an indirect one, and that the experimental errors in both determinations are reflected in the final figures, the results are satisfactory.

TABLE III. ANALYSES OF MOLASSES AND SIRUPS								
No.	Source	Combined Method		Reducing Sugars as Invert Sugar				$\frac{S-P}{I}$
		Total reducing sugars	Dextrose in reducing sugars	Old M. and W. Table		New M. and W. Table		
				Gravi-metric	Volumetric	Gravi-metric	Volumetric	
Raw Sugar Blackstraps								
10	Cuba	12.31	29.3	12.38	12.06	12.43	12.11	0.569
18	Cuba	15.84	33.2	15.73	15.54	15.81	15.63	0.630
26	Cuba	10.96	26.1	10.80	10.69	10.83	10.72	0.753
2	Puerto Rico	24.41	48.0	25.03	24.18	25.20	24.31	0.218
4	Puerto Rico	20.11	40.0	19.74	19.86	19.81	19.99	0.458
15	Puerto Rico	21.81	40.3	22.34	21.54	22.49	21.67	0.354
1	Sto. Domingo	14.43	35.5	14.25	14.20	14.31	14.26	0.532
3	Sto. Domingo	23.12	47.3	22.87	22.95	23.02	23.10	0.312
11	Sto. Domingo	14.45	29.3	14.08	14.20	14.14	14.26	0.692
14	India	16.61	49.2	17.00	16.53	17.11	16.62	0.253
23	Java	21.05	48.8	21.21	20.93	21.34	21.07	0.269
16	Philippines	22.81	59.3	...	22.85	...	22.99	0.348
Av., omitting No. 16	Av. No.	...	40.5	...	...	...	...	0.447
High-Test Molasses								
6	Cuba	56.60	49.8	56.71	56.29	57.04	56.60	0.273
7	Cuba	42.91	50.7	42.46	42.74	42.71	43.00	0.268
8	Cuba	58.51	48.1	58.17	58.13	58.51	58.47	0.307
9	Cuba	58.71	48.5	58.49	58.37	58.83	58.70	0.351
12	Cuba	62.27	55.2	61.40	62.12	61.70	62.53	0.230
17	Cuba	41.63	51.7	41.06	41.48	41.34	41.74	0.253
5	Barbados	31.51	53.2	31.49	31.51	31.63	31.66	0.299
	Av.	50.31	51.0	49.97	50.09	50.25	50.39	0.273
Refinery Blackstraps								
19		18.75	55.0	...	18.73	...	18.86	...
20		21.50	56.2	...	21.50	...	21.63	...
22		26.84	56.7	...	26.84	...	26.98	...
24		23.39	55.5	...	23.37	...	23.50	...
	Av.	22.62	55.8	...	22.61	...	22.74	...
Refinery Filtered Sirups								
21		19.57	57.4	...	19.60	...	19.73	...
23		23.69	58.9	...	23.73	...	23.87	...
25		28.55	57.1	...	28.55	...	28.72	...
	Av.	23.94	57.8	...	23.96	...	24.11	...

The new method was next applied to the analysis of molasses and sirups from various sources, with the results shown in Table III. The third column in this table gives the percentage of total reducing sugars (dextrose plus levulose), and the fourth the percentage of dextrose in the reducing sugars. It is noted that in the raw sugar blackstraps, with the exception of No. 16, this percentage is below 50, and in some cases much lower; the average figure is 40.5. The average for the high-test molasses (partially

inverted sirups) is much higher, 51.0, although in some individual cases it runs below 50. This would indicate that the acid inversion process in the factory tends to destroy some of the levulose, as would be expected. In order to prove this definitely, however, it would be necessary to determine dextrose and levulose in the sirup before and after it is inverted in the manufacturing process.

TABLE IV. COMPARISON BETWEEN MUNSON AND WALKER GRAVIMETRIC METHOD AND LANE AND EYNON VOLUMETRIC METHOD			
No	Reducing Sugars as Invert Sugar		Method of Lane and Eynon %
	Method and table of Munson and Walker %		
	Raw Sugar Blackstraps		
	High-Test Molasses		
27	19.90		19.74
28	16.39		15.68
29	23.22		22.52
30	17.59		17.24
31	12.17		12.09
33	17.59		17.24
34	19.48		19.07
35	15.61		15.31
39	18.72		18.72
40	19.23		19.25
41	18.29		18.13
46	18.87		18.83
47	22.21		20.78
48	20.13		19.74
	Av. 18.53		18.17
32	30.07		29.48
36	32.75		32.86
37	55.64		55.00
38	46.36		46.30
42	50.00		48.58
43	49.08		49.50
44	49.31		49.30
45	66.30		65.20
49	53.50		55.80
50	31.64		31.78
51	37.80		36.74
52	55.29		55.50
53	39.16		38.64
54	51.23		50.46
55	46.78		45.93
56	33.75		32.94
57	36.26		37.20
	Av. 44.99		44.78

An idea of the proportion between dextrose and levulose may be gained also from Browne's "polarizing constant" (2), which is the ratio of  $S - P$  to  $R$ , where  $S$  is the sucrose determined by the optical method with invertase,  $P$  the direct polarization, and  $R$  the total reducing sugars, usually expressed as invert sugar. The raw sugar blackstraps and high-test molasses listed in Table III, excepting No. 16, had been received by this laboratory for routine trade analyses, and the sucrose determinations were therefore made by the U. S. Treasury method and not by the invertase method. For this reason the polarizing constants shown in the last column of Table III are only approximate, but they are nevertheless useful for a comparison with the ratio of dextrose to total reducing sugars, given in column 3. A polarizing constant of about 0.3 denotes equal parts of dextrose and levulose; when the levulose is higher than the dextrose the polarizing constant rises above 0.3, and it decreases below 0.3 when the dextrose is higher than the levulose. The figures in the last column of the table show that most of the blackstraps have a polarizing constant above 0.3, with an average of 0.447, while in the high-test molasses the constant is in most cases below 0.3, with an average of 0.273, thus confirming the results obtained by the combined reduction method as to the ratio between dextrose and levulose.

The refinery blackstraps and filtered sirups were analyzed only by the combined reduction method. The blackstraps show a distinct excess of dextrose over levulose, and the filtered sirups a still greater one. This corroborates the general observation that levulose is removed in the refinery process, particularly by treatment with bone black.



TABLE V. MILLIGRAMS OF LEVULOSE CORRESPONDING TO MILLIGRAMS OF CUPRIC OXIDE OR COPPER, AND REDUCING RATIOS *a*  
For varying proportions of dextrose and levulose in presence of sucrose (0.4 gram of total sugars in 50 ml. of solution), by Munson and Walker method

CuO	Cu	Levulose	Reducing Ratio, <i>a</i> , for Varying Proportions between <i>D</i> and <i>L</i>										Proportions between <i>D</i> and <i>L</i>									
			100 <i>D</i>					90 <i>D</i>					80 <i>D</i>					70 <i>D</i>				
			0 <i>L</i>	10 <i>L</i>	20 <i>L</i>	30 <i>L</i>	40 <i>L</i>	50 <i>L</i>	60 <i>L</i>	70 <i>L</i>	80 <i>L</i>	90 <i>L</i>	0 <i>L</i>	10 <i>L</i>	20 <i>L</i>	30 <i>L</i>	40 <i>L</i>	50 <i>L</i>	60 <i>L</i>	70 <i>L</i>	80 <i>L</i>	90 <i>L</i>
50	39.9	18.3	1.119	1.121	1.123	1.125	1.127	1.129	1.127	1.127	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
52	41.5	19.1	1.119	1.121	1.123	1.125	1.127	1.129	1.127	1.127	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
54	43.1	20.0	1.119	1.121	1.123	1.125	1.127	1.129	1.127	1.127	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
56	44.7	20.9	1.118	1.120	1.122	1.124	1.126	1.128	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
58	46.3	21.7	1.118	1.120	1.122	1.124	1.126	1.128	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
60	47.9	22.6	1.118	1.120	1.122	1.124	1.126	1.128	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
62	49.5	23.5	1.117	1.120	1.122	1.124	1.126	1.128	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
64	51.1	24.3	1.117	1.120	1.122	1.124	1.126	1.128	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
66	52.7	25.2	1.116	1.119	1.121	1.124	1.126	1.128	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
68	54.3	26.1	1.116	1.119	1.121	1.124	1.126	1.128	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
70	55.9	27.0	1.116	1.119	1.121	1.124	1.126	1.128	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
72	57.5	27.9	1.115	1.118	1.120	1.123	1.125	1.127	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
74	59.1	28.7	1.115	1.118	1.120	1.123	1.125	1.127	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
76	60.7	29.6	1.115	1.118	1.120	1.123	1.125	1.127	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
78	62.3	30.5	1.114	1.117	1.119	1.122	1.125	1.127	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
80	63.9	31.4	1.114	1.117	1.119	1.122	1.125	1.127	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
82	65.6	32.3	1.113	1.116	1.118	1.121	1.124	1.127	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
84	67.1	33.2	1.113	1.116	1.118	1.121	1.124	1.127	1.126	1.126	1.125	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124	1.124
86	68.7	34.1	1.112	1.115	1.117	1.120	1.123	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
88	70.3	35.0	1.112	1.115	1.117	1.120	1.123	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
90	71.9	35.8	1.112	1.115	1.117	1.120	1.123	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
92	73.5	36.7	1.111	1.114	1.116	1.119	1.122	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
94	75.1	37.6	1.111	1.114	1.116	1.119	1.122	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
96	76.7	38.4	1.111	1.114	1.116	1.119	1.122	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
98	78.3	39.3	1.111	1.114	1.116	1.119	1.122	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
100	79.9	40.2	1.111	1.114	1.116	1.119	1.122	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
102	81.5	41.1	1.111	1.114	1.116	1.119	1.122	1.125	1.124	1.124	1.123	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122	1.122
104	83.1	42.0	1.110	1.113	1.115	1.118	1.121	1.124	1.123	1.123	1.122	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121
106	84.7	42.9	1.110	1.113	1.115	1.118	1.121	1.124	1.123	1.123	1.122	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121
108	86.3	43.8	1.110	1.113	1.115	1.118	1.121	1.124	1.123	1.123	1.122	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121
110	87.9	44.7	1.110	1.113	1.115	1.118	1.121	1.124	1.123	1.123	1.122	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121	1.121
112	89.5	45.6	1.109	1.112	1.114	1.117	1.120	1.123	1.122	1.122	1.121	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120
114	91.1	46.5	1.109	1.112	1.114	1.117	1.120	1.123	1.122	1.122	1.121	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120
116	92.7	47.4	1.109	1.112	1.114	1.117	1.120	1.123	1.122	1.122	1.121	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120
118	94.3	48.2	1.109	1.112	1.114	1.117	1.120	1.123	1.122	1.122	1.121	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.120
120	95.9	49.1	1.108	1.111	1.113	1.116	1.119	1.122	1.121	1.121	1.120	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119
122	97.5	50.0	1.108	1.111	1.113	1.116	1.119	1.122	1.121	1.121	1.120	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119
124	99.1	50.9	1.108	1.111	1.113	1.116	1.119	1.122	1.121	1.121	1.120	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119
126	100.7	51.8	1.108	1.111	1.113	1.116	1.119	1.122	1.121	1.121	1.120	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119	1.119
128	102.3	52.7	1.107	1.110	1.112	1.115	1.118	1.121	1.120	1.120	1.119	1.118	1.118	1.118	1.118	1.118	1.118	1.118	1.118	1.118	1.118	1.118
130	103.9	53.6	1.107	1.110	1.112	1.115	1.118	1.121	1.120	1.120	1.119	1.118	1.118	1.118	1.118	1.118	1.118	1.118	1.118	1.118	1.118	1.118



160	127.8	67.0	1.103	1.106	1.109	1.112	1.115	1.117	1.118	1.119	1.121	1.122	1.123	1.124	1.125	1.126	1.127	1.128	1.129	1.130	1.131	1.132	1.133	1.134	1.135	1.136	1.137	1.138	1.139	1.140	1.141	1.142	1.143	1.144	1.145	1.146	1.147	1.148	1.149	1.150	1.151	1.152	1.153	1.154	1.155	1.156	1.157	1.158	1.159	1.160	1.161	1.162	1.163	1.164	1.165	1.166	1.167	1.168	1.169	1.170	1.171	1.172	1.173	1.174	1.175	1.176	1.177	1.178	1.179	1.180	1.181	1.182	1.183	1.184	1.185	1.186	1.187	1.188	1.189	1.190	1.191	1.192	1.193	1.194	1.195	1.196	1.197	1.198	1.199	1.200	1.201	1.202	1.203	1.204	1.205	1.206	1.207	1.208	1.209	1.210	1.211	1.212	1.213	1.214	1.215	1.216	1.217	1.218	1.219	1.220	1.221	1.222	1.223	1.224	1.225	1.226	1.227	1.228	1.229	1.230	1.231	1.232	1.233	1.234	1.235	1.236	1.237	1.238	1.239	1.240	1.241	1.242	1.243	1.244	1.245	1.246	1.247	1.248	1.249	1.250	1.251	1.252	1.253	1.254	1.255	1.256	1.257	1.258	1.259	1.260	1.261	1.262	1.263	1.264	1.265	1.266	1.267	1.268	1.269	1.270	1.271	1.272	1.273	1.274	1.275	1.276	1.277	1.278	1.279	1.280	1.281	1.282	1.283	1.284	1.285	1.286	1.287	1.288	1.289	1.290	1.291	1.292	1.293	1.294	1.295	1.296	1.297	1.298	1.299	1.300	1.301	1.302	1.303	1.304	1.305	1.306	1.307	1.308	1.309	1.310	1.311	1.312	1.313	1.314	1.315	1.316	1.317	1.318	1.319	1.320	1.321	1.322	1.323	1.324	1.325	1.326	1.327	1.328	1.329	1.330	1.331	1.332	1.333	1.334	1.335	1.336	1.337	1.338	1.339	1.340	1.341	1.342	1.343	1.344	1.345	1.346	1.347	1.348	1.349	1.350	1.351	1.352	1.353	1.354	1.355	1.356	1.357	1.358	1.359	1.360	1.361	1.362	1.363	1.364	1.365	1.366	1.367	1.368	1.369	1.370	1.371	1.372	1.373	1.374	1.375	1.376	1.377	1.378	1.379	1.380	1.381	1.382	1.383	1.384	1.385	1.386	1.387	1.388	1.389	1.390	1.391	1.392	1.393	1.394	1.395	1.396	1.397	1.398	1.399	1.400	1.401	1.402	1.403	1.404	1.405	1.406	1.407	1.408	1.409	1.410	1.411	1.412	1.413	1.414	1.415	1.416	1.417	1.418	1.419	1.420	1.421	1.422	1.423	1.424	1.425	1.426	1.427	1.428	1.429	1.430	1.431	1.432	1.433	1.434	1.435	1.436	1.437	1.438	1.439	1.440	1.441	1.442	1.443	1.444	1.445	1.446	1.447	1.448	1.449	1.450	1.451	1.452	1.453	1.454	1.455	1.456	1.457	1.458	1.459	1.460	1.461	1.462	1.463	1.464	1.465	1.466	1.467	1.468	1.469	1.470	1.471	1.472	1.473	1.474	1.475	1.476	1.477	1.478	1.479	1.480	1.481	1.482	1.483	1.484	1.485	1.486	1.487	1.488	1.489	1.490	1.491	1.492	1.493	1.494	1.495	1.496	1.497	1.498	1.499	1.500	1.501	1.502	1.503	1.504	1.505	1.506	1.507	1.508	1.509	1.510	1.511	1.512	1.513	1.514	1.515	1.516	1.517	1.518	1.519	1.520	1.521	1.522	1.523	1.524	1.525	1.526	1.527	1.528	1.529	1.530	1.531	1.532	1.533	1.534	1.535	1.536	1.537	1.538	1.539	1.540	1.541	1.542	1.543	1.544	1.545	1.546	1.547	1.548	1.549	1.550	1.551	1.552	1.553	1.554	1.555	1.556	1.557	1.558	1.559	1.560	1.561	1.562	1.563	1.564	1.565	1.566	1.567	1.568	1.569	1.570	1.571	1.572	1.573	1.574	1.575	1.576	1.577	1.578	1.579	1.580	1.581	1.582	1.583	1.584	1.585	1.586	1.587	1.588	1.589	1.590	1.591	1.592	1.593	1.594	1.595	1.596	1.597	1.598	1.599	1.600	1.601	1.602	1.603	1.604	1.605	1.606	1.607	1.608	1.609	1.610	1.611	1.612	1.613	1.614	1.615	1.616	1.617	1.618	1.619	1.620	1.621	1.622	1.623	1.624	1.625	1.626	1.627	1.628	1.629	1.630	1.631	1.632	1.633	1.634	1.635	1.636	1.637	1.638	1.639	1.640	1.641	1.642	1.643	1.644	1.645	1.646	1.647	1.648	1.649	1.650	1.651	1.652	1.653	1.654	1.655	1.656	1.657	1.658	1.659	1.660	1.661	1.662	1.663	1.664	1.665	1.666	1.667	1.668	1.669	1.670	1.671	1.672	1.673	1.674	1.675	1.676	1.677	1.678	1.679	1.680	1.681	1.682	1.683	1.684	1.685	1.686	1.687	1.688	1.689	1.690	1.691	1.692	1.693	1.694	1.695	1.696	1.697	1.698	1.699	1.700	1.701	1.702	1.703	1.704	1.705	1.706	1.707	1.708	1.709	1.710	1.711	1.712	1.713	1.714	1.715	1.716	1.717	1.718	1.719	1.720	1.721	1.722	1.723	1.724	1.725	1.726	1.727	1.728	1.729	1.730	1.731	1.732	1.733	1.734	1.735	1.736	1.737	1.738	1.739	1.740	1.741	1.742	1.743	1.744	1.745	1.746	1.747	1.748	1.749	1.750	1.751	1.752	1.753	1.754	1.755	1.756	1.757	1.758	1.759	1.760	1.761	1.762	1.763	1.764	1.765	1.766	1.767	1.768	1.769	1.770	1.771	1.772	1.773	1.774	1.775	1.776	1.777	1.778	1.779	1.780	1.781	1.782	1.783	1.784	1.785	1.786	1.787	1.788	1.789	1.790	1.791	1.792	1.793	1.794	1.795	1.796	1.797	1.798	1.799	1.800	1.801	1.802	1.803	1.804	1.805	1.806	1.807	1.808	1.809	1.810	1.811	1.812	1.813	1.814	1.815	1.816	1.817	1.818	1.819	1.820	1.821	1.822	1.823	1.824	1.825	1.826	1.827	1.828	1.829	1.830	1.831	1.832	1.833	1.834	1.835	1.836	1.837	1.838	1.839	1.840	1.841	1.842	1.843	1.844	1.845	1.846	1.847	1.848	1.849	1.850	1.851	1.852	1.853	1.854	1.855	1.856	1.857	1.858	1.859	1.860	1.861	1.862	1.863	1.864	1.865	1.866	1.867	1.868	1.869	1.870	1.871	1.872	1.873	1.874	1.875	1.876	1.877	1.878	1.879	1.880	1.881	1.882	1.883	1.884	1.885	1.886	1.887	1.888	1.889	1.890	1.891	1.892	1.893	1.894	1.895	1.896	1.897	1.898	1.899	1.900	1.901	1.902	1.903	1.904	1.905	1.906	1.907	1.908	1.909	1.910	1.911	1.912	1.913	1.914	1.915	1.916	1.917	1.918	1.919	1.920	1.921	1.922	1.923	1.924	1.925	1.926	1.927	1.928	1.929	1.930	1.931	1.932	1.933	1.934	1.935	1.936	1.937	1.938	1.939	1.940	1.941	1.942	1.943	1.944	1.945	1.946	1.947	1.948	1.949	1.950	1.951	1.952	1.953	1.954	1.955	1.956	1.957	1.958	1.959	1.960	1.961	1.962	1.963	1.964	1.965	1.966	1.967	1.968	1.969	1.970	1.971	1.972	1.973	1.974	1.975	1.976	1.977	1.978	1.979	1.980	1.981	1.982	1.983	1.984	1.985	1.986	1.987	1.988	1.989	1.990	1.991	1.992	1.993	1.994	1.995	1.996	1.997	1.998	1.999	2.000
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The routine analyses referred to above included also determinations of reducing sugars by the gravimetric Munson and Walker method, the results being reported as invert sugar, on the basis of the original Munson and Walker tables. The figures obtained are shown in column 5 of Table III. For the purpose of direct comparison, the results of the volumetric determinations have been recalculated and expressed as invert sugar, on the basis of the original Munson and Walker tables. Owing to the pressure of routine work it was usually not possible to run the volumetric determinations at the same time as the gravimetric, and in some cases there was an interval of several weeks, during which time the samples may have undergone slight changes. The comparisons, therefore, do not permit of definite conclusions. Nevertheless, with the blackstraps the results of the volumetric method check in most cases with those of the gravimetric within the limits of error, but in some they are distinctly lower. The average tendency is towards lower results, reflecting the effect of the mineral impurities on the result of the gravimetric method. In the high-test molasses, however, the results of the volumetric method are in several instances distinctly higher than those of the gravimetric and the average tendency is also towards high values. It has been noticed that these high-test molasses are often very acid, and it may therefore be expected that inversion still goes on slowly during storage.

The general tendency of the gravimetric Munson and Walker method to give high results is well illustrated by comparison with the Lane and Eynon volumetric method. These analyses, shown in Table IV, were made with an entirely different series of molasses samples, and the two determinations were run simultaneously, so that the time factor does not enter.

With the blackstraps, the Lane and Eynon method gave lower results in all cases except two, but in these two the figures are not more than 0.02 per cent higher, well within the limit of error. The average Lane and Eynon result is 0.36 per cent lower, or 1.94 per cent on total reducing sugars. With the high-test molasses the average Lane and Eynon figure is only 0.21 per cent lower, or 0.47 per cent on the basis of total reducing sugars. These results are just as would be expected, since the high-test molasses have a much higher total sugar purity than the blackstraps, their ash content is much lower, and the copper precipitate should therefore carry down less mineral matter than in the case of blackstraps. If the results of the gravimetric method are calculated from the new Munson and Walker table of the writers, the figures of the Lane and Eynon method for the blackstraps average 0.45 per cent lower, or 2.42 per cent lower on the basis of the total reducing sugars; for the high-

test molasses they average 0.48 per cent lower, or 1.06 per cent on the total reducing sugars.

If the Munson and Walker method is retained as an official method for the analysis of molasses, the copper in the precipitate should be determined by a convenient method, either volumetric or electrolytic. Much time could be saved, without sacrificing accuracy, by substituting the Lane and Eynon method for that of Munson and Walker.

### Summary and Conclusions

The reducing effect of dextrose only, and of levulose only, in the presence of sucrose, on Fehling solution has been determined for the method of Munson and Walker, and the results are given in the form of a table. By combining this method for the determination of total reducing sugars with that of Jackson and Mathews for the determination of apparent levulose, the dextrose and the levulose can be calculated from the two equations. Check analyses gave satisfactory results. Application of the method to the analysis of various types of molasses and sirups has shown that in raw sugar blackstraps the levulose usually exceeds the dextrose; in inverted (high-test) molasses, however, the dextrose is generally higher than the levulose, part of the latter being destroyed during the manufacturing process. Refinery blackstraps contain a lower proportion of levulose than invert molasses, and filtered refinery sirups a still lower one. The gravimetric Munson and Walker method gives too high results for reducing sugars, no matter whether the precipitate is weighed as oxide or after reduction to metal, because of the mineral impurities carried down by the precipitate. It is suggested that either the copper be determined by a volumetric or electrolytic method, or that the Lane and Eynon method be substituted for the Munson and Walker method.

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PLANT OF THE AMERICAN POTASH AND CHEMICAL CORPORATION, TRONA, CALIF.



# Estimation of Degree of Souring in Sugar-Cane Juice

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Because of variations in the normal acidity of cane from different sugar-cane varieties and from different fields, and also the differences in normal acidity due to the degree of topping, the total acidity shown by soured juices gives a poor indication of the excess acidity produced by the souring. The determination of the excess acidity formed in the cane after damage by freezing can be approximated from the final pH, the amount of the drop in pH, or by a simple distillation test. The comparative values for the excess acidity, pH, and pH drop obtained during the past season in Louisiana are given, and the distillation test is described. The use of excess acidity rather than total acidity values is recommended for the evaluation of deteriorated cane.

**D**ETERIORATION of sugar cane following the severe freezes of the recent Louisiana harvest made it desirable for factory operators to have a method for evaluating the cane for milling. The common commercial practice was to determine total titrated acidity of the crusher juices of hand-mill samples. Operators realized that this basis was far from ideal, but it was the only practicable measuring stick they could use. Knowing that total acidity was not a very satisfactory criterion, preliminary experiments were carried out at the Houma Field Station in search of a better one. Fortunately, suitable material was available in connection with windrowing experiments, since tests were possible on sound cane, before deterioration started, and later with corresponding samples of soured cane. By sound cane is meant cane either before freezing or immediately after freezing before souring occurred.

It is now generally known that the acidity of juices from sound cane varies widely because of varietal characteristics, soil effects, fertilization, climate, and other factors. In a particular locality the normal acidity may vary from 1.5 to 3.0 cc., but for the entire sugar belt the range is more nearly 0.7- to 4.5-cc. acidity. This being the case, it is evident that total acidity cannot be a very satisfactory basis for the estimation of degree of deterioration following freezing. For example, of two lots of cane of 4.0-cc. acidity, one may be sound cane in which the high acidity is due to normal conditions of growth, while the other may be soured cane that originally had low acidity. If acidity is a measure of the condition of frozen cane, then only the acidity produced by the deterioration can properly be considered. For the purposes of this discussion, the acidity formed by souring will be called "excess acidity." It is not certain to what extent excess acidity is a measure of the quality of the cane from the viewpoint of factory operations, but it is certain to be a much more accurate basis than total acidity. At least, it is a true measure of the degree of

souring. The question, however, as to whether souring is directly correlated with degree of gum formation will not be discussed at this time.

## Excess Acidity versus pH

In spite of the considerable variation in the total acidity of normal cane juices from different varieties and fields, it has nevertheless been found that in a particular locality the variation in pH is very small, and even in the entire sugar belt the range is not large. For example, in a given locality the variation is likely to be about 0.2 pH, say from 5.30 to 5.50 pH, and for the whole Louisiana sugar-producing area the range is probably only from 5.2 to 5.6 pH. Because of the relatively constant pH of normal cane juices, pH values below 5.20 give an immediate indication of souring. The correlation of pH and the pH drop with excess acidity was extensively studied during the past season, and while the amount of information obtained may not permit the absolute estimation of excess acidity, it is sufficient for the purpose of estimating the approximate amount of excess acidity in grading the cane. As the measurement of pH is comparatively convenient and speedy, it is especially suited to control work.

The equipment used was a commercial glass-electrode pH electrometer, but the quinhydrone electrode, although slower to use, is otherwise satisfactory. The pH and electrometrically titrated acidity were determined immediately after the freeze and subsequently on duplicate samples of juice from windrowed and standing cane at different stages of souring. The principal studies were made on the varieties Co. 281 and Co. 290, but limited tests on all commercial varieties were included. The windrow tests were conducted in the Houma area. The data obtained were examined from two viewpoints, (1) the exactness with which the pH value indicated the degree of souring independent of the initial pH of the sound cane, and (2) the relation between the amount of the drop in pH and excess acidity. The excess acidity was the difference between the acidity of the sound cane juice and that of the corresponding soured samples after storage.

TABLE I. VALUES FOR pH AND pH DROP VERSUS EXCESS ACIDITY

Excess Acidity <sup>a</sup> Cc.	pH Value	Drop in pH
0.5	5.05-5.15	0.2-0.3
1.0	4.85-5.05	0.3-0.5
1.5	4.70-4.85	0.5-0.7
2.0	4.55-4.70	0.7-0.8
2.5	4.45-4.55	0.8-0.9
3.0	4.40-4.45	0.9-1.0
3.5	4.35-4.40	1.0-1.1
5.0	4.10-4.20	1.1-1.2
7.0	3.95-4.05	1.3-1.4

<sup>a</sup> Cc. of 0.1 N alkali for 10 cc. of juice.

It was found that when souring had proceeded to the extent of developing about 1.0-cc. excess acidity or more, the correlation between pH and excess acidity was a definite factor. When the souring was very slight, the pH was influenced by the initial pH of the sound cane and the degree of souring was uncertain unless the normal pH was known for comparison. For the range of 1.0- to 3.0-cc. excess acidity, which some operators believe are the limits within which deteriorated cane can possibly be handled reasonably well in the factory, the final pH determination gives a fair measure of the degree of



souring. A comparison of pH and excess acidity is given in Table I. As more widespread information is accumulated in the future, it may be found that the comparative values will not agree exactly with those obtained in this preliminary study.

### Excess Acidity versus pH Drop

If the initial pH of the sound cane is known, the drop in pH can be estimated from the pH value of the soured cane. This was the case in these experiments, but in the factory it is possible only when the average pH of the cane supply is known. The pH of the juice during the normal part of the season is likely to be uniform, unless the cane is from widely separated areas, and if a number of samples are tested during this period, the average pH established is likely to be close to the pH of the normal cane remaining in the fields. The drop below this value after a freeze may then be interpreted as excess acidity with somewhat greater accuracy than is possible from a single determination of the final pH value of the soured cane. This is especially true in the range of excess acidity below 1.0 cc. The relation of drop in pH to excess acidity (as found in these experiments) is also shown in Table I.

### Excess Acidity by Distillation

Since most of the acidity formed by the souring is acetic acid; which is volatile with steam (while the normal acids of sugar-cane juice are nonvolatile), it is possible to estimate the excess acidity by a distillation method. A simple distillation setup of a 300-cc. flask connected with a condenser is all that is required. For complete distillation of the volatile acids the flask has to be equipped with a dropping funnel for the addition of water, or with a live steam jet. From the preliminary tests, however, it appears likely that complete distillation of the volatile acids is not needed to obtain a fair estimate of the excess acidity. The procedure suggested is to distill off 25 cc. from a 100-cc. juice sample and titrate the distillate in the usual manner with 0.1 N alkali, using phenolphthalein as indicator. The value thus obtained was found to be a good approximation of the excess acidity of 10 cc. of juice—that is, roughly 10 per cent of the total excess acidity in the 100-cc. sample distilled over in the first 25 cc. of condensate, which is equivalent to the excess acidity in 10 cc. of juice.

In the preliminary work the distillations were made on juices the excess acidity of which was known. The distillate was collected and titrated in 25-cc. portions until essentially complete distillation of the volatile acids was obtained. It was noted that the first 25 cc. of condensate indicated the amount of the excess acidity in the manner just described. The total volatile acids agreed with the known excess acidity when the degree of souring was relatively slight, especially under 1.0 cc. of excess acidity. When the souring was extreme not all the excess acidity could be recovered by distillation, and it is assumed that as the souring progresses there are possibly nonvolatile acids formed to some extent in addition to the acetic acid. That such may be the case is also indicated by some experiments where the drop in pH was measured after additions of 0.1 N acetic acid to sound cane juice. The pH obtained with acetic acid agreed with that from the same degree of souring up to roughly 2 cc. of excess acidity, but beyond that point the pH drop due to souring was greater than that found for the corresponding amounts of acetic acid, indicating the presence of acids stronger than acetic in the soured juice. These might be acids such as malic, oxalic, or tartaric which are stronger acids than acetic, are nonvolatile, and have been found in other fermentation products.

When souring is slight, the titration of the first 25 cc. of distillate from a 100-cc. sample of juice is a better measure of

excess acidity than is the pH determination. Sound cane juice gives no titratable acids in the distillate until the sample is practically boiled dry, and then only a trace. So even a little acid in the first 25 cc. of condensate is a sure sign of souring and indicates approximately the amount of excess acidity. It is to be clearly understood that the values thus obtained by distillation are not absolute measures of excess acidity, yet they are satisfactory for practical purposes, and with standardization of equipment and method may become rather exact.

TABLE II. SECTIONING TESTS ON NORMAL AND SOURED CANE

	Initial Acidity Cc.	Total Acidity after Souring Cc.	Excess Acidity Cc.
Whole cane (normally topped)	2.21	3.50	1.29
Cane topped back one-third (average of bottom two-thirds)	1.58	2.69	1.11
Top third section	2.74	5.60	2.86
Middle third section	1.86	3.48	1.62
Bottom third section	1.30	1.90	0.60

On first consideration a distillation test of this kind may appear too cumbersome for routine factory control, but as it is possible to set up 10 or more of the simple distillation outfits in a rather compact manner, and, as the distillation required is brief, it is believed that one operator may be able to test a hundred or more samples per day. This method is better than the pH determination (1) because it does not require any assumption as to the original, normal pH or acidity of the juice—in short, it is specific for the volatile acids produced by souring; (2) because it gives a more accurate value for small amounts of souring, detecting even traces; and (3) because the cost of laboratory equipment is less. The pH procedure of estimating excess acidity has the advantage in speed and in space required for the equipment, and is considered just as accurate for amounts of excess acidity above 1.0 cc. Both methods can doubtless be improved as further studies are made, but even at the present stage of development either can be used to put the evaluation of frozen cane on the better basis of excess acidity rather than on that of total acidity.

### Effect of Low Topping

The use of the excess acidity instead of the total acidity determination as a measure of souring is justified not only because of the variation in the normal acidity of the whole cane but also because of the practice of severely topping back cane which shows souring. This cutting back is sometimes essential in order to obtain juices of higher purity and to save the better part of deteriorated cane for milling, when it may not be possible to save the entire crop; but it further complicates the interpretation of total acidity as a measure of deterioration because of the much lower normal acidity of cane topped in this manner. When soured cane is topped back a third or more, the relatively low acidity of the milled portion may actually include an unsuspected and considerable proportion of excess acidity. The experience at factories where juice of moderate total acidity gave trouble in processing can possibly be explained on this basis. Taking as an example one of the sectioning tests made on Co. 281 windrowed after the first freeze (Table II), there should be noted (1) the difference between the normal acidity of the sections, (2) the contrast between the acidity of the normally topped whole cane and that of cane which has been topped back a third, (3) the moderate total acidity of the bottom two-thirds (2.69 cc.) when the total acidity of the normally topped cane was high (3.50 cc.), and (4) the high excess acidity in the bottom two-thirds in spite of the moderate total acidity.



Not all damaged cane sours over its entire length, as was the case with this particular test; the degree of damage probably is an important factor. It is, however, likely that much of the frozen cane ground during the past season, which had been severely topped back, was moderately high in excess acidity even when, on the basis of total acidity, it appeared satisfactory for processing.

An alternate explanation of poor factory operation with juices of moderate total acidity lies in the possibility that gum formation may proceed without the corresponding for-

mation of excess acidity. It is not known at present to what extent the formation of gums and acids is correlated. Much more information is needed before the evaluation of frozen and soured cane can be put on an entirely fair and accurate basis. The estimation of excess acidity, however, should be a forward step, as it affords a better means of determining actual souring in cane.

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# Determination of Alpha- and Beta-Carotenes

## By Means of the Spectrophotometer and the Photoelectric Photometer

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BECAUSE of the relationship of carotene and vitamin A and the difference in vitamin A potency of  $\alpha$ - and  $\beta$ -carotenes, the accurate quantitative determination of the carotenes is of considerable importance. Colorimetric methods (1, 8) were used early for the determination of carotene and are still used extensively (3, 7, 9, 12). Schertz (10) found the spectrophotometric method more accurate than the colorimetric method. Although, when proper precautions are taken, accurate results may be obtained with the colorimetric method, the spectrophotometric method has the additional advantage that no standard solution is needed for comparison. It is necessary only to determine the absorption coefficient for pure carotene in the solvent to be used at the wave-length setting for the particular instrument used. The solvent chosen must be one in which carotene obeys Beer's law. Shrewsbury and Kraybill (11) and Barnett (2) have shown that carotene dissolved in fat does not obey Beer's law.

In this paper are reported the values of the absorption coefficients for  $\alpha$ - and  $\beta$ -carotenes dissolved in heptane at two wave-length settings for the Bausch & Lomb spectrophotometer with definite light source and slit width adjustments. A comparison was made of the accuracy of determination of  $\alpha$ - and  $\beta$ -carotenes by the spectrophotometric and the photoelectric photometric methods.

### Experimental

Alpha- and  $\beta$ -carotenes were prepared by the procedure of Miller (5). All solvents used were repurified. An impure mixture of the carotenes (secured from the S. M. A. Corporation, Cleveland, Ohio) was dissolved in light petroleum ether and separated by passing through a column of calcium hydroxide 10 cm. (4 inches) high and 7.5 cm. (3 inches) in diameter. The layers containing the  $\alpha$ - and  $\beta$ -carotenes were separated and the carotenes eluted with a 2 per cent solution of methyl alcohol in petroleum ether. Final separation and purification were effected by again passing the carotenes through calcium hydroxide columns. After elution from the calcium hydroxide the carotenes were concentrated at a low temperature *in vacuo*, crystallized from petroleum ether, dried in a desiccator, and stored in evacuated ampules. The following constants were obtained:

	Melting Point Corrected ° C.	Hydrogen %	Carbon %
$\alpha$ -Carotene	178.5	10.38	89.23
$\beta$ -Carotene	177.8	10.34	88.94

Theoretically carotene ( $C_{40}H_{56}$ ) contains 9.93 per cent of hydrogen and 90.07 per cent of carbon.

Samples of the carotenes were analyzed for purity by the spectrophotoelectric method. The following results were obtained:  $\alpha$ -carotene,  $96.0 \pm 1.0$  per cent;  $\beta$ -carotene,  $97.4 \pm 1.0$  per cent; impurities colorless.

Calculations of the concentration of the carotene solutions used in this study were based on the purity of the carotenes as shown by the above analyses.

In previous work (4, 11) carotene determinations were made with the spectrophotometer by the method of Schertz (10) at wave length 435.8  $m\mu$ , using light from a 1000-watt incandescent bulb. It is difficult to read transmittancies under these conditions because of the low light sensitivity of the eye and the low intensity of an incandescent lamp in that region. In order to overcome this difficulty the absorption spectra of  $\alpha$ - and  $\beta$ -carotenes were determined to obtain a suitable wave length that would afford a greater light intensity. The results are reproduced in Figure 1, which shows that  $\alpha$ -carotene dissolved in heptane exhibits maximum absorption at 447.5 and 475  $m\mu$  and  $\beta$ -carotene at 455 and 480  $m\mu$ . These maximum absorption points agree closely in wave lengths with those reported by Miller, Mackinney, and Zscheile (6) for  $\alpha$ - and  $\beta$ -carotenes dissolved in alcohol and ether. In the work that follows 450 and 475  $m\mu$  were selected as wave lengths for the determination of  $\alpha$ -carotene and 455 and 480  $m\mu$  for  $\beta$ -carotene.

TECHNIC. A stock solution of the carotene was prepared by weighing out 10 to 15 mg. of the material on the microbalance. This was made to volume with purified heptane and the five to eight solutions to be examined were prepared by dilution. Heptane was used as a solvent in preference to petroleum ether because loss of solvent by evaporation could thus be reduced materially. The solutions were examined immediately after preparation with the spectrophotometer and photoelectric photometer. A 2-cm. cell was used with the spectrophotometer with the majority of solutions. However, when the depth of color was low the 10-cm. cell was employed. One- and 2-cm. rectangular cells were used with the photoelectric photometer. The depths of the cells were measured accurately and corrections were applied in the calculations of transmittancies.



TABLE I.  $\alpha$  VALUES OF  $\alpha$ - and  $\beta$ -CAROTENES AT VARIOUS CONCENTRATIONS  
(Photoelectric photometer)

Carotene Concentration Mg./l.		$\alpha$ -Carotene		$\beta$ -Carotene		Carotene Concentration Mg./l.		$\alpha$ -Carotene		$\beta$ -Carotene	
		-Log T	$\alpha$	-Log T	$\alpha$			-Log T	$\alpha$	-Log T	$\alpha$
0.4		0.079	196.8	0.080	199.6	3.0		0.556	185.4	0.578	192.8
0.5		0.098	196.4	0.100	199.4	3.1		0.573	184.8	0.596	192.4
0.6		0.118	196.1	0.120	199.1	3.2		0.590	184.3	0.615	192.1
0.7		0.137	195.6	0.140	198.8	3.3		0.606	183.7	0.633	191.8
0.8		0.156	195.3	0.160	198.7	3.4		0.623	183.2	0.651	191.4
0.9		0.175	194.9	0.179	198.4	3.5		0.639	182.6	0.669	191.1
1.0		0.194	194.5	0.198	198.2	3.6		0.656	182.1	0.687	190.7
1.1		0.214	194.1	0.218	198.0	3.7		0.672	181.6	0.704	190.4
1.2		0.232	193.7	0.238	197.7	3.8		0.688	181.1	0.721	189.7
1.3		0.251	193.3	0.258	197.5	3.9		0.704	180.5	0.740	189.7
1.4		0.270	192.7	0.277	197.2	4.0		0.720	180.0	0.757	189.3
1.5		0.289	192.4	0.297	197.0	4.1		0.736	179.5	0.776	188.9
1.6		0.307	192.0	0.315	196.7	4.2		0.751	178.8	0.792	188.6
1.7		0.326	191.5	0.334	196.4	4.3		0.767	178.3	0.809	188.2
1.8		0.344	191.2	0.353	196.1	4.4		0.782	177.7	0.826	187.8
1.9		0.362	190.7	0.372	195.9	4.5		0.797	177.2	0.843	187.4
2.0		0.381	190.3	0.392	195.6	4.6		0.813	176.7	0.860	187.0
2.1		0.399	189.8	0.411	195.4	4.7		0.827	176.0	0.877	186.6
2.2		0.416	189.3	0.431	195.1	4.8		0.842	175.5	0.894	186.2
2.3		0.434	188.9	0.448	194.8	4.9		0.857	174.9	0.910	185.8
2.4		0.452	188.4	0.467	194.5	5.0		0.872	174.3	0.927	185.4
2.5		0.470	188.0	0.486	194.2	5.1		0.886	173.7	0.944	185.0
2.6		0.488	187.5	0.504	194.0	5.2		0.900	173.1	0.960	184.6
2.7		0.505	187.0	0.523	193.7	5.3		0.914	172.4	0.976	184.2
2.8		0.522	186.5	0.542	193.4	5.4		0.928	171.8	0.993	183.8
2.9		0.539	185.9	0.560	193.0	5.5		0.942	171.3	1.009	183.5

Photoelectric Photometer

The photoelectric photometer used in this work was described by Withrow, Shrewsbury, and Kraybill (13).

The absorption curves obtained with the spectrophotometer were used as an aid in selecting the proper filter system for the carotenes (Figure 1). The specific absorption coefficients for the solutions examined were calculated according to the formula  $\alpha = 1000t/cl$ , where  $c$  is the concentration of carotene in milligrams per liter,  $t$  the  $-\log$  of the transmittancy,  $T$ , and  $l$  the depth of the cell in centimeters. Specific absorption coefficients for carotene concentrations of successive 0.5 mg. per liter intervals were plotted (Figure 2). More usable data are presented in Table I which gives the  $-\log$  of the transmittancies and the  $\alpha$  values for concentrations of from 0.4 to 5.5 mg. of carotene per liter.

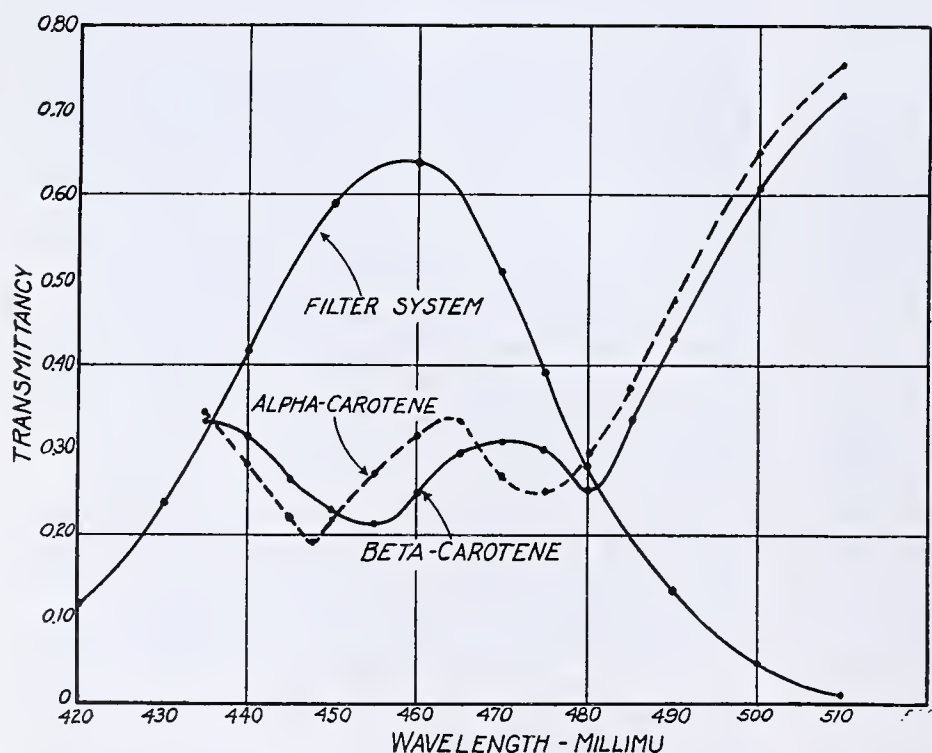


FIGURE 1. TRANSMISSION CURVES OF  $\alpha$ - AND  $\beta$ -CAROTENES AND FILTER SYSTEM OF PHOTOELECTRIC PHOTOMETER

Jena glass filter system = BG 12 and GG 5. 10-cm. (4-inch) depth, 5 per cent copper sulfate

An examination of Figure 2 and Table I shows that as the concentration increases the  $\alpha$  values decrease. On account of the wide band of light used with the photoelectric photometer a straight-line relationship does not exist between carotene concentration and transmittancy as it does with the spectrophotometer. However, where extreme accuracy is not required the relationship is sufficiently linear between carotene concentrations of 0.5 and 2.5 mg. per liter to permit the use of the average  $\alpha$  values. These are 192.2 for  $\alpha$ -carotene and 196.8 for  $\beta$ -carotene. The use of these values will introduce an error of less than 2 per cent with  $\beta$ -carotene and less than 3 per cent with  $\alpha$ -carotene.

Table I facilitates the calculation of the concentration of unknown solutions by furnishing the correct  $\alpha$  value to be used for any given measured transmittancy ( $-\log T$ ). Table

II contains data checking the accuracy of determinations of  $\beta$ -carotene by means of the photoelectric photometer. These data were calculated by using the  $\alpha$  values of Table I and were made several months after the original data had been obtained.

Solutions 1 to 11 were made from  $\beta$ -carotene from carrots separated and purified in the authors' own laboratory from an impure mixture of  $\alpha$ - and  $\beta$ -carotenes (secured from the S. M. A. Corporation, Cleveland, Ohio). Solutions 12 to 15 were prepared from a sample of pure  $\beta$ -carotene from barley leaves furnished through the courtesy of H. H. Strain.

Inspection of Table II shows that  $\beta$ -carotene can be determined with a high degree of accuracy by means of the photoelectric photometer. The errors of most of the determinations were less than 1.0 per cent.

The use of the photoelectric photometer in the determination of carotene has the advantage that it is as accurate as the spectrophotometer and that the equipment is relatively cheaper. It is also rapid and not subject to personal errors such as are obtained in matching colors in the spectrophotometer with the human eye.



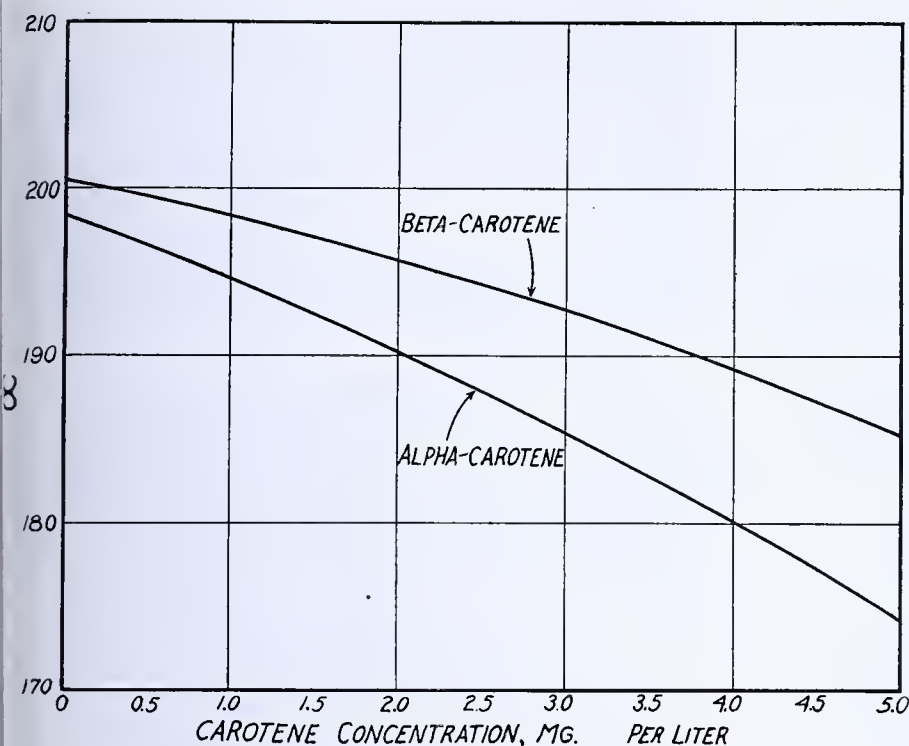


FIGURE 2. SPECIFIC ABSORPTION COEFFICIENTS OF  $\alpha$ - AND  $\beta$ -CAROTENES AT DIFFERENT CONCENTRATIONS  
Photoelectric photometer

TABLE II. ACCURACY OF PHOTOELECTRIC PHOTOMETER

Solution Number	(β-carotene)		Error of Determination Mg./l.	Error %
	Carotene Theoretical Mg./l.	Carotene Found Mg./l.		
1	0.442	0.439	-0.0030	-0.67
2	0.884	0.897	+0.0130	+1.47
3	1.326	1.333	+0.0070	+0.52
4	1.768	1.776	+0.0080	+0.45
5	2.210	2.227	+0.0170	+0.76
6	2.652	2.679	+0.0270	+1.01
Av.				+0.59
7	0.4231	0.4190	-0.0041	-0.96
8	0.8462	0.8507	+0.0045	+0.53
9	1.2693	1.2526	-0.0167	-1.32
10	1.6924	1.6850	-0.0074	-0.43
11	2.1155	2.1193	+0.0038	+0.17
Av.				-0.40
12 <sup>a</sup>	0.6432	0.6377	-0.0055	-0.85
13 <sup>a</sup>	0.9648	0.9582	-0.0066	-0.68
14 <sup>a</sup>	1.2864	1.2707	-0.0157	-1.22
15 <sup>a</sup>	1.6080	1.6005	-0.0075	-0.46
Av.				-0.80

<sup>a</sup> Sample of pure  $\beta$ -carotene from barley leaves prepared by and furnished through the courtesy of H. H. Strain, Division of Plant Biology, Carnegie Institute of Washington, Stanford, Calif.

### The Spectrophotometer

A Bausch & Lomb spectrophotometer with a 1000-watt projection lamp as light source was employed. This equipment permits the easy measurement of transmittancies in a 2-cm. cell of carotene solutions of concentrations between 0.5 and 3.0 mg. per liter at about 450 m $\mu$  and between 0.5 and 3.0 mg. per liter at about 480 m $\mu$ . Concentrations higher than these absorb so much light that matching is difficult or impossible and concentrations lower than these are too light a color to obtain accurate matches.

The spectroscopy collimating slit and eyepiece slit were set on the third scale division when readings were made between wave lengths 400 and 460 m $\mu$  [slit width of entrance slit (collimator) 0.3 mm.; of exit slit (eye-piece) 0.9 mm.]. When readings were made at longer wave lengths the eye-piece slit was set on the third division and the collimating slit on the second division [slit width of entrance slit (collimator) 0.2 mm.; of exit slit (eye-piece) 0.9 mm.].

In the spectrophotometric work two observers made readings at both wave lengths on all the solutions. The average of the two sets of readings was used in the calculation of the specific absorption coefficients. Specific absorption coefficients ( $\alpha$  values) were calculated for the solutions at two wave lengths according to the formula used above.

The following average specific absorption coefficients were found:  $\alpha$ -carotene, 246.4 at 450 m $\mu$ , 223.6 at 475 m $\mu$ ;  $\beta$ -carotene, 240.4 at 455 m $\mu$ , 210.0 at 480 m $\mu$ .

Figure 3 shows the results obtained when the logarithms of the transmittancies are plotted against carotene concentrations. A straight-line relationship holds which indicates that carotene in heptane obeys Beer's law.

The accuracy of determinations calculated from the specific absorption coefficients given above can be seen from an examination of Table III, which contains the results from a study of fifteen carotene solutions. It shows that the errors of determination were larger and not as constant as in the case of the photoelectric photometer. Although the average error was small, the variation between different samples was large.

An average error of about 1.0 per cent was found.

Visual spectrophotometric determinations vary considerably because of the natural difficulty in matching colors. While this is usually not large enough to be of serious consequence, for practical purposes it increases the error above that found with instruments where the eye is not a factor.

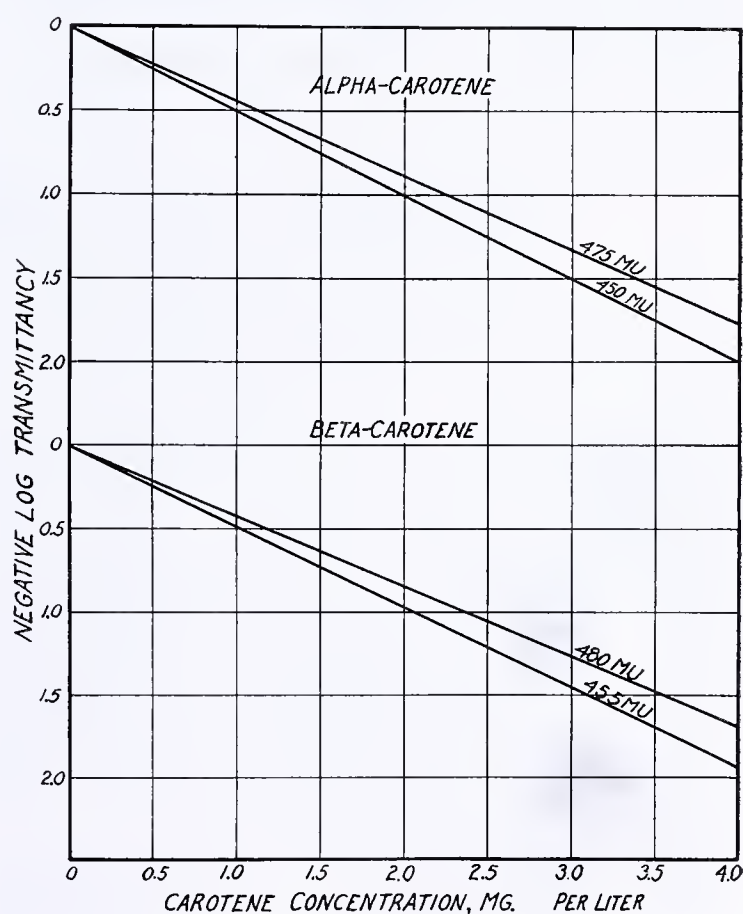


FIGURE 3. TRANSMITTANCIES OF  $\alpha$ - AND  $\beta$ -CAROTENES AT WAVE LENGTHS OF MAXIMUM ABSORPTION

Measurements calculated on 2-cm. cell basis. Each curve is a composite of several determinations on solutions of similar concentration.



TABLE III. DETERMINATION OF CAROTENES BY MEANS OF SPECTROPHOTOMETER

Solution Num- ber	Wave Length 455 m $\mu$				Wave Length 480 m $\mu$			
	Carotene theoreti- cal Mg./l.	Carotene found Mg./l.	Error of determina- tion Mg./l.	Error %	Carotene found Mg./l.	Error of determina- tion Mg./l.	Error %	
<b><math>\beta</math>-Carotene</b>								
1	0.7569	0.7877	+0.0308	+4.06	0.7689	+0.0120	+1.58	
2	0.8127	0.8231	+0.0104	+1.27	0.8306	+0.0179	+2.20	
3	1.1354	1.1702	+0.0348	+3.06	1.1510	+0.0156	+1.37	
4	1.1746	1.1723	-0.0023	-0.19	1.1724	-0.0022	-0.18	
5	1.3441	1.2887	-0.0554	-4.12	1.3100	-0.0341	-2.53	
6	1.5138	1.5485	+0.0347	+2.29	1.5497	+0.0359	+2.36	
7	1.8925	1.9497	+0.0572	+3.02	1.9199	+0.0274	+1.44	
8	1.9577	1.9580	+0.0003	+0.02	1.9532	-0.0045	-0.22	
9	2.0318	2.0266	-0.0052	-0.25	2.0505	+0.0187	+0.92	
10	2.2707	2.3384	+0.0677	+2.98	2.3210	+0.0503	+2.21	
11	2.4381	2.4693	-0.0312	-1.27	2.5014	+0.0633	+2.59	
12	3.1363	3.0848	-0.0515	-1.64	3.0591	-0.0772	-2.46	
Av.	....	....	+0.0075	+0.769	....	+0.0102	+0.77	
<b><math>\alpha</math>-Carotene</b>								
1	0.4253	0.4298	+0.0045	+1.05	0.4006	-0.0247	-5.80	
2	0.7623	0.7527	-0.0096	-1.25	0.7591	-0.0032	-0.41	
3	0.8509	0.8859	+0.0350	+4.11	0.8102	-0.0407	-4.78	
4	0.8814	0.8526	-0.0288	-3.26	0.8002	-0.0812	-9.21	
5	1.0165	1.0009	-0.0156	-1.53	1.0217	+0.0052	+0.51	
6	1.1386	1.1623	+0.0237	+2.08	1.1753	+0.0367	+3.22	
7	1.2706	1.2713	+0.0007	+0.06	1.2643	-0.0063	-0.49	
8	1.2764	1.3359	+0.0595	+4.66	1.2977	+0.0213	+1.66	
9	1.3220	1.3117	-0.0103	-0.77	1.2565	-0.0655	-4.95	
10	1.7628	1.7718	+0.0090	+0.51	1.7273	-0.0355	-2.01	
11	2.1274	2.1754	+0.0480	+2.25	2.1481	+0.0207	+0.97	
12	2.2034	2.2258	+0.0224	+1.01	2.1903	-0.0131	-0.59	
13	2.5528	2.5871	+0.0343	+1.34	2.5398	-0.0130	-0.50	
14	2.6440	2.6799	+0.0359	+1.35	2.6400	-0.0040	-0.15	
15	2.8465	2.9018	+0.0553	+1.94	2.8893	+0.0428	+1.50	
Av.	....	....	+0.0176	+0.83	....	+0.0107	-1.40	

### Conclusions

Data are presented on the determination of  $\alpha$ - and  $\beta$ -carotenes by means of the photoelectric photometer and the spectrophotometer.

The carotenes can be determined with an accuracy of about 1 per cent with the photoelectric photometer or the spectrophotometer. The variation in the error is greater with the spectrophotometer.

The use of heptane rather than a petroleum ether of low

boiling point as a solvent reduces the change in concentration of the solutions through evaporation during examination.

Alpha-carotene in heptane exhibits maximum absorption of light at 447.5 and 475 m $\mu$ ,  $\beta$ -carotene at 455 and 480 m $\mu$ . Spectrophotometric readings at these wave bands are made without difficulty, using the 1000-watt incandescent lamp as a light source.

Specific absorption coefficients have been calculated for  $\alpha$ - and  $\beta$ -carotenes at various concentrations for use with the photoelectric photometer and the spectrophotometer at specified settings of slit widths.

### Acknowledgments

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## Solutions for Colorimetric Standards

### Permanent Series for the *o*-Tolidine Method for Chlorine

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SINCE its adoption by the American Public Health Association for the determination of residual chlorine in drinking water, the *o*-tolidine method has been the object of considerable study. Until now, however, no spectrophotometric data on the oxidized *o*-tolidine yellow or on the various permanent color standards have appeared. The recording spectrophotometer is particularly suited for this kind of work because it furnishes a permanent record, free from all subjective interpretations, that may be used for later comparison. An attempt was made in this work to study the nature of the *o*-tolidine yellow, including the effect of hydrogen-ion concentration upon it, and to determine which of the proposed standards presents the best color match.

The yellow color that is produced on treating an aqueous solution of chlorine with *o*-tolidine is accepted as being the result of an oxidation process. Various factors, such as temperature, time of contact between chlorine and reagent, presence or absence of bright light, and hydrogen-ion concentra-

tion, are known to affect the nature as well as the intensity of the color that is obtained. Of these factors, the proper control of the hydrogen-ion concentration has been least appreciated.

### Reagents

The *o*-tolidine used was of Eastman Kodak grade. A 0.1 per cent solution in 10 per cent (by volume) hydrochloric acid was prepared according to the approved A. P. H. A. method (2). This solution is designated as the "standard" *o*-tolidine reagent. "Double-strength" reagent was prepared by using 20 per cent acid. All *o*-tolidine solutions were stored in the dark.

Standard chlorine water was obtained by diluting a stock solution which was prepared by the absorption of reagent grade gaseous chlorine in distilled water. The concentration of the solution (approximately 13 p. p. m.) was determined by titration with standard sodium thiosulfate (approximately 0.025 *N*). The disappearance of the blue starch color at the end point was made more distinct by transferring the solution being titrated to a 100-ml. Nessler tube and comparing with a suitable blank. The standard solution was kept in a black bottle, fitted to a microburet with glass connections, to facilitate the removal of measured

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volumes of solution with minimum loss of chlorine to the outside air. The separate solutions of the "temporary" standards (0.01 to 2.0 p. p. m.) were prepared from this standard solution by dilution of measured amounts with "zero" water.

Zero water, or water showing no chlorine demand, was prepared by the method of Adams and Buswell (1), with the exception that the doubly distilled water was acidified with 3 ml. of concentrated hydrochloric acid before the chlorine overs dosage. The prior acidification seemed to increase the thoroughness with which the chlorine demand of the distilled water was removed. Fresh samples of such water were made each day.

The permanent standards and buffer solutions were made from recrystallized material according to the directions given in the literature.

### Apparatus

A photoelectric spectrophotometer, of the type described by Hardy (6), was used in the determination of all transmittancy data. The adjustment of this instrument was checked against readings of a mercury arc and Bureau of Standards glasses. All measurements were made in 5-cm. cells.

Both the photoelectric color comparator, used in much of the preliminary work, and the vacuum tube pH meter, used in all pH measurements, have been described previously (8).

Plane-bottom Nessler tubes, with the 100-ml. mark 30 cm. from the bottom, were used in visual comparison tests.

### Experimental Work

McCrum has shown (7) that *o*-tolidine in the oxidized form acts as a neutralization indicator, its hue changing from yellow to blue through the pH range 2.0 to 3.5. From this it is apparent that varying shades of *o*-tolidine yellow will be produced unless the final pH of the solution is constant or lies outside the range of color change. The A. P. H. A. method (2) specifies the use of 1 ml. of *o*-tolidine reagent (10 per cent hydrochloric acid by volume) per 100 ml. of water tested, this amount being assumed to provide a satisfactory pH value. Experiments show, however, that this amount of acid is hardly sufficient. Thus a sample of tap water having pH of 7.67 was treated with 1 ml. of the standard reagent and the resultant solution had a pH of 2.24. Probably a more alkaline water, or one of greater hardness, would show a pH as high as 2.5 after treatment.

The result of this variation in final pH is shown in the transmittancy curves in Figure 1. The light absorption throughout the range of 560 to 700 m $\mu$  (curve 5) indicates the greenish yellow hue of the *o*-tolidine solution that results whenever the color is developed in the range of pH 2.0 to 2.5. The magnitude of the variation becomes far more evident when the data are calculated for a 30-cm. cell length, which corresponds to the depth of solution used in ordinary Nessler tube comparisons. The nature of the true *o*-tolidine yellow desired is shown by curve 4. It is apparent that a reproducible hue of the desired color is obtained only when the final pH of the solution is below 2.

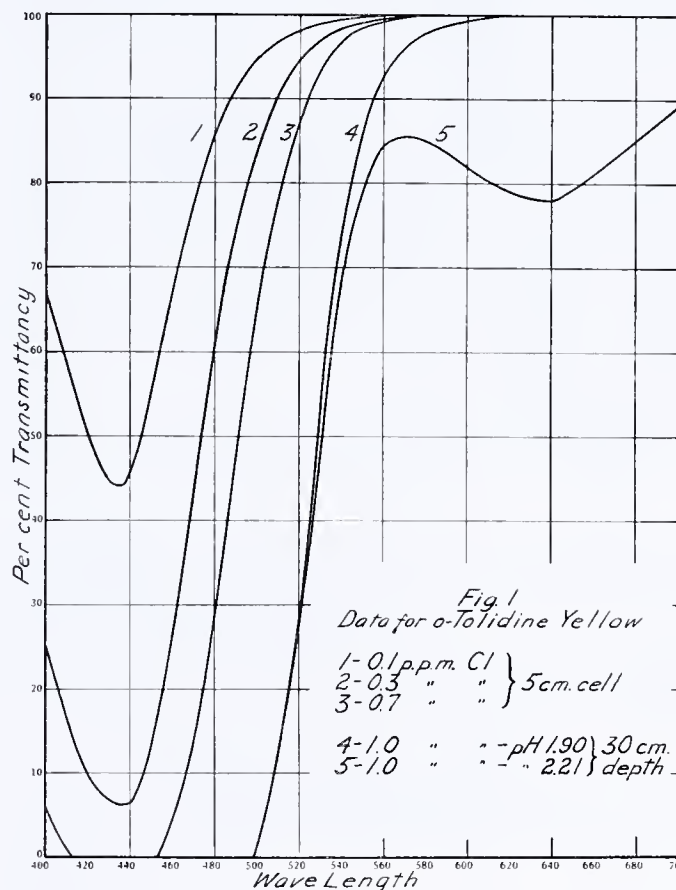
The obvious solution to the problem is to use 2 ml. of the standard reagent or 1 ml. of the double-strength reagent, as suggested by McCrum, per 100 ml. of test solution. In the large majority of cases this will ensure a final pH value that is below the region of color change.

With this factor in mind, the temporary standards were prepared and their transmittancy curves obtained. Recommendations regarding temperature, time of contact, and development of the color in the dark were observed, as given by the American Public Health Association (2). Fading during the time of measurement was very small, as the solution in the spectrophotometer was about 3 meters from the light source and the data were obtained within 15 minutes after the solution was prepared. The nature of the data is shown in curves 2, 3, and 4 of Figure 1. Two points in particular are to be observed: Each transmittancy curve shows a minimum at

436 m $\mu$ ; and there is no absorption of light through the region 560 to 700 m $\mu$ . These items are of importance in the later discussion.

### Permanent Standards

Because of the instability of the oxidized *o*-tolidine yellow and the difficulty of making up standards of known chlorine content, the estimation of unknown amounts necessitates the preparation of inorganic permanent standards, visually equivalent to the color produced by the chlorine-*o*-tolidine reaction.

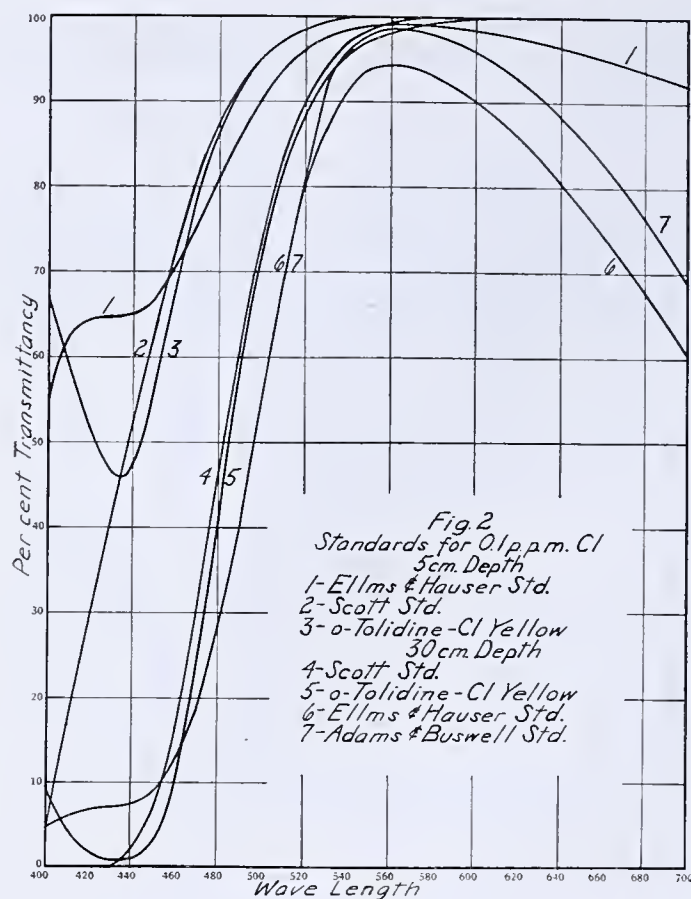


The first of these sets of permanent standards was prepared by Ellms and Hauser (5). They used acidified stock solutions of potassium dichromate and cupric sulfate, the individual standards being prepared by mixing small volumes of the stock solutions and diluting them to 100 ml. with distilled water. Comparison with unknowns was made in 30-cm. Nessler tubes. Muer and Hale (9), unable to verify this work, proposed another set which contained larger amounts of the same stock solutions. However, they specified 24-cm. Nessler tubes, the necessity for which remained unexplained. Adams and Buswell (1) suggested a third set which is in virtual agreement with that of Ellms and Hauser. Donahue and Zimbon (4) and Daniels (3) prepared other sets for use with small thickness of solutions. The first of these uses 32-mm. depths, and the second three depths—13, 26, and 51 mm.—with a different standard for each depth. All the above permanent standards are made from the same stock solutions and differ only in the amounts used.

Scott (10), noting the troublesome specification of tube length and the variation in composition of the solutions, prepared a set of standards that could be used irrespective of tube length. He used a potassium chromate-dichromate mixture, buffered at pH 6.5.

A comparison of certain selected spectrophotometric data for these different standards, with their chlorine equivalents, is shown in Figure 2. Curves 4, 6, and 7 represent data for the Scott, Ellms and Hauser, and Adams and Buswell standards, respectively, for a chlorine concentration of 0.1 p. p. m. The corresponding transmittancy data for the *o*-tolidine





yellow are given by curve 5. All these data are given on a 30-cm. basis. A comparison of the Muer and Hale, the Donahue and Zimbon, and the Daniels standards is shown in Table I. These data correspond to 24-cm., 32-mm., and 51-mm. depths, respectively.

TABLE I. TRANSMITTANCIES

(Muer and Hale, Donahue and Zimbon, and Daniels standards and the corresponding temporary standards)

Wave Length Mμ	Per Cent Transmittancy					
	Muer and Hale	Tempo- rary	Donahue and Zimbon	Tempo- rary	Daniels	Tempo- rary
400	2.4	15.2	24.2	49.6	42.8	42.0
420	7.0	4.3	36.7	31.0	53.7	53.0
440	7.6	2.8	37.4	26.5	53.8	46.8
460	12.6	15.7	46.2	52.0	61.4	67.5
480	28.9	49.1	62.4	77.7	74.0	85.9
500	57.1	77.4	80.6	91.7	86.7	94.6
520	84.3	90.8	93.4	97.2	95.2	97.9
540	96.8	96.3	98.4	99.5	98.4	99.1
560	99.8	98.7	98.7	99.9	99.2	99.4
580	98.3	100.0	98.4	99.9	99.5	99.9
600	96.3	100.0	97.1	99.9	99.2	99.9
640	88.6	100.0	92.8	99.9	97.5	99.9
680	76.2	100.0	84.8	99.9	94.0	99.9
700	68.8	100.0	80.1	99.9	92.4	99.9

Comparison of the colorimetric data of the inorganic standards with their chlorine equivalents shows two striking differences. First, the permanent standards do not show the characteristic minimum at 436 mμ, which is peculiar to the *o*-tolidine yellow and would be difficult to duplicate. Fortunately, this difference occurs in the far blue where the sensitivity of the eye is very low. A second difference occurs in the region 600 to 700 mμ where all the permanent standards, with the exception of Scott's, show absorption due to the copper sulfate. It is apparent from the transmittancy curves that the chromate-dichromate mixtures of Scott present the best match, both in the form of the curve and in the agreement in the per cent transmittancy.

Curves 1, 2, and 3 of Figure 2 represent the transmittancy data of the Ellms and Hauser, the Scott, and the temporary standards, respectively, for 0.1 p. p. m. and a 5-cm. cell. Apart from the difference in the far blue, the agreement be-

tween the Scott and the temporary standard is good. The disagreement between the Ellms and Hauser and the temporary standard is marked, although probably not serious visually. From the agreement of the Scott and the temporary standards at both 5- and 30-cm. tube lengths, it is obvious that this set of permanent standards can be used irrespective of tube length.

A complete comparative study of the Scott standards and their chlorine equivalents revealed agreement in transmittancy curves throughout the range 0.1 to 2 p. p. m. Below 0.1 p. p. m. there were discrepancies, the Scott standards containing insufficient amounts of the chromate-dichromate stock solution. Because of these differences, a modification of the standards is proposed, as indicated in Table II.

TABLE II. MODIFIED SCOTT STANDARDS

Chlorine P. p. m.	Stock Solution	
	Present Ml.	Proposed Ml.
0.10	4.4	4.4
0.07	2.8	3.1
0.05	1.9	2.2
0.03	1.1	1.3
0.02	0.7	0.8
0.01	0.3	0.4

It is clear from the lack of relationship between the volumes of solution required to make up the permanent standards that the *o*-tolidine-chlorine yellow does not obey Beer's law.

Visual comparison of the various standards was made, but, because of the nature of the work, positive conclusions are very difficult. The authors were unable to differentiate between any of the standards and the corresponding *o*-tolidine yellow equivalent, when using the tube length for which these standards were designed. When comparisons were attempted at other tube lengths, it was very obvious that the permanent standards, with the exception of Scott's, did not present a colorimetric match. This interesting fact seems to be due to the peculiar balance between the absorption in the red and the blue regions at the tube length for which the standard was designed. It does not hold for comparisons at other tube lengths. The Scott standards, since they follow the *o*-tolidine absorption more closely, matched equally well at all tube lengths.

## Conclusions

This spectrophotometric study of the *o*-tolidine method for chlorine shows (1) the colorimetric characteristics of the *o*-tolidine yellow, including the desirability of having the final pH below 2, and (2) the relation between the various permanent standards and their *o*-tolidine yellow equivalents. The Scott standards are considered the best, although the others are visually satisfactory, provided the specification regarding tube length is followed.

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# Determination of Fluorine Spray Residue on Tomatoes

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THE aim of this paper is not to present a perfected method of analysis for fluorine in tomatoes but rather to describe some of the difficulties encountered in the application of the Willard and Winter titration method (6), using the Armstrong (2) modification to employ sodium alizarin sulfonate as indicator, and the chloroacetic acid buffer of Hoskins and Ferris (5). The merits of sulfuric and of perchloric acids for the distillation of fluorine are compared for pure fluorine solutions and for ashed samples of fluorine-bearing tomatoes, and a distillation procedure is suggested to utilize the merits of the two.

## Solutions and Chemicals

**SODIUM ALIZARIN SULFONATE SOLUTION.** Dissolve 0.050 gram of sodium alizarin sulfonate in 100 ml. of water.

**SODIUM FLUORIDE SOLUTIONS.** 0.01 mg. of fluorine per ml. Weigh 2.2105 grams of c. p. sodium fluoride and make up to 1 liter. Prepare a standard by diluting 10.00 ml. of this solution to 1 liter.

**THORIUM NITRATE SOLUTION.** Dissolve 0.4579 gram of c. p.  $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$  in water and make up to 1 liter.

**CHLOROACETIC BUFFER (5), 0.24 M.** Dissolve 22.7 grams of monochloroacetic acid to give 100 ml. of solution. Neutralize 50 ml. with 6 N sodium hydroxide, combine two portions, and make up to 1 liter.

**MAGNESIUM OXIDE, C. P.,** low in fluorine.

**SILVER PERCHLORATE SOLUTION (1).** Adjust concentration so that 1 ml. is equivalent to 0.02 gram of sodium chloride.

## Titration

To the sample to be titrated (not exceeding 12.5 ml. in volume) in a 50-ml. beaker are added 15 ml. of 95 per cent ethanol, 0.10  $\pm$  0.01 ml. of 0.05 per cent sodium alizarin sulfonate, and water to make 27.5 ml. The color of the indicator is adjusted with 0.5 N sodium hydroxide and 0.5 N hydrochloric acid until it has a pure yellow color without excess of acid. Then 2.5 ml. of 0.24 M chloroacetic buffer are added and the solution is titrated with thorium nitrate solution using a 5-ml. microburet. It is assumed that the volume of 0.5 N hydrochloric acid or sodium hydroxide will not disturb the final volume more than about 1 ml. The end point is taken when the color matches that of a blank to which has been added exactly 0.05 ml. of the thorium nitrate solution. As the end point is approached the sample and standard are transferred to 50-cc. Nessler tubes in which more accurate matching of colors is possible than in the original beakers. The 50-ml. beakers are preferable initially, however, because of greater facility of mixing. The Nessler tubes should be illuminated from the bottom by a uniformly white surface receiving its light preferably from the blue sky, and never direct sunlight.

Because the red colored lake so produced is not stable, and appreciably intensifies in color after an hour or two, it has been found desirable to substitute for it a permanent color. This may be accomplished by matching the end-point color, above described, with an aqueous solution of cobalt nitrate and potassium bromate. The red and yellow colors from these two salts are easily adjusted to give a solution which has the same intensity and shade as the original thorium-alizarin sulfonate lake. Titrations of pure sodium fluoride solutions made in this manner are reproducible to about 0.01 ml. with the given concentrations.

As long as pure sodium fluoride is being titrated, the end points are satisfactory. The larger titrations show somewhat more vague color transitions, but no more than is compensated for by the greater volume of thorium nitrate solution to measure; hence the relative accuracy is about the same for titrations varying from 1 to 3 ml., which is the most satisfactory range. As many workers have reported, various ions can seriously interfere. The most common anions encountered

are sulfate, perchlorate, carbonate, and chloride. The effect of these ions has been previously reported by tabulating limiting concentrations below which they do not seriously interfere. To clarify this matter, Table I shows the quantitative effect of these ions in various amounts under the standard titration conditions when titrating sodium fluoride solutions.

TABLE I. QUANTITATIVE EFFECT OF INTERFERING IONS

[Net (gross - 0.05) titrations for NaF using chloroacetic acid buffer (5) in presence of various ions. Total volume 30 ml., 50% in 95%  $\text{C}_2\text{H}_5\text{OH}$ ]

Interfering Substance <sup>a</sup>	0.00 Mg. F Ml.	0.02 Mg. F Ml.	0.05 Mg. F Ml.	0.10 Mg. F Ml.	0.15 Mg. F Ml.
None	0.00	0.20	0.69	1.46	2.19
$\text{H}_2\text{SO}_4$	0.10 0.25	0.02 0.04	0.23 0.26	0.76 0.81	1.56 1.63
HCl	5.0 10.0	..	..	..	2.17 2.15
$\text{HClO}_4$	10.0 20.0 30.0	..	..	..	2.19 2.18 2.18
$\text{BaCl}_2$	0.05 0.10	..	..	..	1.40 1.37
$\text{H}_2\text{CO}_3$	20.0 100.0	..	..	..	1.47 1.44
No buffer, 30-ml. volume	0.00	..	..	..	1.46
5 ml. extra $\text{H}_2\text{O}$	0.00	..	..	..	1.46
No buffer, 5 ml. extra $\text{H}_2\text{O}$	0.00	..	..	..	1.38

<sup>a</sup> Acids all added as the sodium salt.

Barium chloride is included, since an attempt to use it for the removal of sulfate might be considered. The last three items in the table illustrate the value of the buffer in greatly reducing the error arising from volumes of solution differing from the standard volume. This furnishes an argument for its use in addition to the claim of convenience and accuracy advanced by the originators.

## Preparation of Sample for Distillation

In a 150-mm. porcelain evaporating dish are placed 100 grams of finely ground tomatoes, 1 gram of magnesium oxide of low fluorine content is thoroughly incorporated, and the mixture is slowly evaporated to dryness overnight on the water bath without stirring or other disturbance. It is then baked for 2 to 3 hours at 135° C. in an oven and finally transferred directly to the muffle furnace regulated at 500° C. The dishes at this point are provided with sheet-iron plates for covers, which are removed at the end of 2 minutes, when danger of loss of flying particles is over. Ashing is then allowed to proceed to a total time of 15 minutes, with some admission of air to burn the carbon. The dishes are then removed and cooled, and 50 ml. of water are added. The carbon is scraped loose from the sides of the dish and any lumps are crushed. Finally the whole is evaporated to dryness, heated for 30 minutes at 135° C., and returned to the muffle, again provided with the sheet-iron covers for the first 2 or 3 minutes to avoid loss by decrepitation. The covers are then removed and ashing is continued with some inlet of air until 15 minutes have elapsed, when the dishes are removed and allowed to cool.

This procedure has been found to give ash practically free of carbon with a total of only 30 minutes of ashing at 500° C. The ash, moreover, is easily handled in transferring it to the distilling flask. Chlorides, which in tomatoes vary from the natural content of about 0.05 per cent to a maximum in canned tomatoes of 1 per cent as sodium chloride, should then be precipitated without delay. For this purpose the ash is taken up as soon as cool in 50 ml. of hot water and silver perchlorate solution (1) is added dropwise. The point of neutralization of chloride has been reached when the brownish or yellowish color of silver oxide makes its appearance throughout the solution and is at least temporarily stable on stirring. If the dishes be allowed to stand



for several hours after cooling, the carbon dioxide of the atmosphere will reduce the pH produced in the ash solution and no brown color will be produced by excess silver perchlorate. The end point must then be obtained by adding a few milliliters of 6 *N* sodium hydroxide prior to the silver perchlorate. The ash mixture is then dried on the water bath and thoroughly transferred to the distilling flask, first with a spatula and then with two 5-ml. portions of water, finally cleaning the dish of all traces of remaining ash with 5 ml. of 6 *N* acid of the kind to be used for the distillation. This distillation in the presence of the silver chloride has been found entirely satisfactory, not giving trouble by bumping, holding back fluorine, or releasing the chloride which it is desired to eliminate. Qualification of this last item must be made in the case of distillation at 160° to 165° C. with sulfuric acid, as the 250-ml. distillate then contains about 10 mg. of hydrochloric acid, which is preferably removed by adding about 1 ml. of the silver perchlorate solution to the distilling flask just before the addition of perchloric acid and start of the second distillation.

### Distillation and Concentration of Distillate

When perchloric acid was used for the distillation, 24 ml. of the acid purified as described below were used, and the temperature was maintained at 135° to 138° C. Sulfuric acid distillations were made with 15 ml. of concentrated c. p. acid and the distillation temperature was held at 160° to 165° C., except in special experiments.

The Willard and Winter (6) distillation apparatus was used. It was found that the insertion into the water tube of a capillary tube of such dimensions that it allowed 4 ml. per minute to flow under a water head of 35 cm. with the stopcock completely open enabled the flow to be adjusted very precisely by raising or lowering the separatory funnel containing the water, so that it often distilled without change of temperature for relatively long periods.

TABLE II. FRACTIONAL DISTILLATIONS  
(2.5 mg. of F by H<sub>2</sub>SO<sub>4</sub> at 135° to 138° C.)

No. of Fraction	Volume of Fraction Ml.	F in Fraction Mg.	Recovery %	Remaining F Distilled into Fraction %
1	25	2.124	84.96	85.0
2	25	0.278	11.12	73.9
3	25	0.040	1.60	40.8
4	25	0.015	0.60	25.9
5	25	0.005	0.20	11.6
6	125	0.021 <sup>a</sup>	0.84	..
Total		2.483	99.32	

<sup>a</sup> Approximate, due to large correction for sulfate error.

The distillate was neutralized with 0.1 *N* sodium hydroxide to a faint pink color with the addition of one drop of phenolphthalein indicator, which does not interfere with the final titration. It was then concentrated to the volume required for titration on a hot plate, preferably with a blast of air blowing into the beaker to effect rapid evaporation without boiling.

### Fractional Distillation

To study the manner in which fluorine distills, a fractional distillation was made by 25-ml. portions from a flask charge of 15 ml. of concentrated sulfuric acid and 25 ml. of sodium fluoride solution containing 0.1 mg. of fluorine per ml. Except on the first fraction, which was diluted fivefold before titration, 10-ml. portions of distillate were titrated. Table II shows the volume of fraction taken, the equivalent net titration of each fraction, the calculated percentage recovery for that fraction, and in the last column, the percentage of the fluorine remaining in the distilling flask at the beginning of a given fraction recovered in that fraction. It is this last column which is of interest. The values rapidly decrease as the volume distilled increases, indicating that it rapidly becomes more difficult to obtain a given percentage of recovery when the total amount of fluorine to be distilled is decreased. Data

given include correction for sulfate error as discussed below. Dahle and Wichmann (3) found that sulfuric acid gives a logarithmic distillation recovery of fluorine; this is at variance with the authors' repeated experience as here illustrated. The cause of the discrepancy is not apparent.

### Contamination during Distillation

In the fluorine analysis of tomato products it is desirable, in order to reduce the size of sample ashed, to concentrate the entire distillate into the final volume of not over 12.5 ml. Using sulfuric acid on distillation this becomes impossible as a variable amount of sulfate averaging approximately 3 mg. of sulfuric acid is contained in 250 ml. of distillate. From the interfering effect of sulfate as given in Table I it is seen, moreover, that an aliquot as small as 10 ml., which contains roughly 0.1 mg. of sulfate, would give a titration of about 107 per cent of the correct value when in the neighborhood of 0.10 mg. of fluorine, with greater error for smaller quantities of fluorine. These observations on sulfate error are in disagreement with published statements declaring sulfuric acid suitable for fluorine distillation, followed by thorium nitrate titration (5). When using perchloric acid under the given conditions of distillation approximately 7 mg. of perchloric acid are carried into the distillate. This quantity, as seen from Table I, will not interfere even when concentrated into one titration. However, c. p. 60 per cent perchloric acid as obtained in two different brands was found to give a blank titration which was not zero when 200 ml. of distillate were concentrated.

The use of rubber stoppers in conjunction with perchloric acid was found to contribute to this failure to obtain a zero blank, which was more nearly approached when glass stoppers were ground in to replace the rubber ones, including the thermometer-capillary tube inlet. The separatory funnel used for the introduction of acid into the flask was replaced by a glass stopper previous to the start of distillation. At the connection of the condenser, the glass tube was merely extended so that it discharged at a point within the water jacket, thus preventing condensate from leaching the cork used to fit the two together. With these precautions it was still found necessary to purify perchloric acid before use by distilling about 350 ml. at 140° C. from 60 ml. of 60 per cent perchloric acid or until experience showed it to yield a substantially zero blank.

TABLE III. RECOVERY OF FLUORINE

	Fluorine Mg.	Net Titration Ml.	Net Theoretical Titration Ml.
1 Direct titration	0.150	2.20	(2.20)
2 Distilled and titrated	0.150	2.22	2.20
3 Ashed sample distilled	0.022	0.41	0.32
4 Second 200 ml.	...	0.35	0.00
5 Third 200 ml. + 0.15 mg. F	...	2.48	2.20
6 Ashed sample distilled	0.10	1.76	1.74
7 Second 200 ml.	...	0.41	0.00
8 Third 200 ml.	...	0.12	0.00
9 Fourth 200 ml.	...	0.27	0.00
10 0.15 mg. F + 1 gram MgO	...	2.45	2.41
11 Second 200 ml.	...	0.09	0.00

All perchloric acid distillations were performed with 24 ml. of purified perchloric acid boiling at 140° C. In one case, 60 ml. of c. p. 60 per cent perchloric acid yielded net titrations on the first and second 250 ml. of purifying distillation of 0.08 ml. and 0.03 ml., the equivalents of roughly 0.005 and 0.002 mg. of fluorine, respectively. While the idea has not been proved, it is suspected that this titration is not due to fluorine, especially since either contaminating stoppers or the ash from a sample of tomatoes causes the titration to continue at a high and irregular level for an indefinite series of 200-ml. fractions. In the absence of organic contamination or of inorganic materials in more than fractional gram quantities, the distilla-



tion of pure sodium fluoride yields results which are equal to direct titration, or slightly higher when deviations are observed. Second distillates in such cases are small, indicating that perchloric acid achieves a nearly quantitative recovery of fluorine and does not introduce the above-described discrepancies when essentially pure sodium fluoride is distilled. These points are illustrated in Table III.

Lines 1 and 2 compare pure sodium fluoride on direct titration and after distillation, concentration, and titration. Lines 3, 4, and 5 are the titrations obtained on distilling a sample composed of 100 grams of tomatoes ashed at 500° C. with 1 gram of c. p. magnesium oxide and found by a double distillation, described below, to contain fluorine equivalent to the titration entered in the third column. This series indicates a greater than 100 per cent recovery on the first 200 ml., a second greater than 100 per cent recovery on the next 200 ml., and a greater than quantitative recovery when 0.15 mg. of fluorine as standard solution was added to the flask for the third 200 ml. Lines 6, 7, 8, and 9 show the series of titrations obtained on four successive 200-ml. distillates from a similarly ashed tomato sample. Here the apparent cumulative recovery amounts to 176 per cent of the known total fluorine content. The conclusion must be drawn that perchloric acid generates a substance which titrates like fluorine when distilling from these heavily salt-laden charges. The end points under these conditions are brownish in color, although reasonably definite. Lines 10 and 11 show results for the distillation of 0.15 mg. of fluorine which had been ashed with 1 gram of magnesium oxide in the absence of tomatoes. The first fraction fairly closely approximated the theoretical, and the titration found for the second fraction was considerably less than experienced when tomato ash was present. The conclusion is that magnesium oxide partly contributes to the effect, but that the tomato ash is the chief offender.

TABLE IV. SINGLE DISTILLATION FROM ASHED SAMPLE  
(200 ml. with HClO<sub>4</sub> at 135° to 138° C. 0.07% = natural salt content of tomatoes used)

Sample No.	Added F Mg.	NaCl %	Net Titration Ml.	Net Titration Minus Blank Ml.	Recovery %
X	0.00	0.07	0.27		
1	0.15	0.50	2.43	2.16	98.2
2	0.15	0.50	2.65	2.38	108.2
3	0.15	0.50	2.48	2.21	100.5
4	0.15	1.00	2.53	2.26	102.6
5	0.15	1.00	2.51	2.24	101.8
6	0.15	0.07	2.45	2.18	99.1
7	0.10	0.07	1.77	1.50	102.0
8	0.10	0.07	1.78	1.51	102.7
9	0.10	0.07	1.76	1.49	101.4
Mean					102.4

Table IV gives the results of analyses of 100-gram samples of tomatoes with fluorine added as sodium fluoride, using a single distillation of 200 ml. with perchloric acid. Various amounts of salt were added. (The "blank" is the analysis of the tomatoes plus magnesium oxide without added fluorine. Both contributed fluorine to this blank, the magnesium oxide being found to contain 12.2 p. p. m. and the tomatoes 0.052 p. p. m of fluorine.)

Under these particular conditions the fluorine found averages about 102.4 per cent. These results would suggest the application of the method to the routine determination of fluorine in tomatoes, bearing in mind that the results depend on the compensation of incomplete distillation by the positive perchlorate error.

Double Distillation

In the effort to eliminate these errors a double distillation was tried, employing sulfuric acid for the first distillation because of its cost, purity, and suitability for high-temperature distillation. The first distillate, 300 ml., was concentrated

as for titration, followed by distillation of 200 ml. with perchloric acid. In the case of the first sulfuric acid fraction, two 200-ml. fractions were taken on the perchloric acid distillation. Table V shows the essential features of this process, being the titrations found on distilling two 300-ml. fractions with sulfuric acid at 145° to 148° C., these fractions being redistilled with perchloric acid to volumes of 200 ml.

TABLE V. DOUBLE DISTILLATION  
(100 grams of tomatoes ashed with 1 gram of MgO and 0.15 mg. of F as NaF)

	Net Titration Ml.
First 300 ml. by H <sub>2</sub> SO <sub>4</sub> at 145–148° C.	
First 200 ml. by HClO <sub>4</sub> , 135–138° C.	2.39
Second 200 ml. by HClO <sub>4</sub> , 135–138° C.	0.01
Second 300 ml. by H <sub>2</sub> SO <sub>4</sub> at 145–148° C.	
First 200 ml. by HClO <sub>4</sub> , 135–138° C.	0.16
Total	2.56
Theoretical recovery = 0.15 mg. F plus blank = 2.52 ml.	
Actual recovery = 2.56 ml. or 102%.	

The cumulative recovery of fluorine is about 102 per cent for all fractions. What is more important, the second perchloric acid distillation of the first sulfuric acid fraction is now very small, indicating that the interfering action noted above with perchloric acid has here nearly disappeared. The interpretation of the titration of the second sulfuric acid fraction is difficult. It may be regarded either as fluorine which escaped distillation into the first fraction, or as being an interference effect similar to that exhibited by perchloric acid. The total recovery observed would suggest that this titration actually represents fluorine, but that a small interfering effect exists, accounting for the excess recovery. The idea of difficulty of recovery of fluorine receives some support from the demonstrated falling off in distillation rate previously shown in Table II, and is in agreement with the observation of Dahle and Wichmann (4) of the restraining effect of salts on the recovery.

A series of analyses was made on 100-gram samples of tomatoes containing amounts of added fluorine of 0.10 mg. and 0.15 mg. by the double distillation described. The sulfuric acid distillation temperature was 160° to 165° C. in the effort to force the fluorine into the first fraction, which was 300 ml. The natural fluorine content of this sample of tomatoes was found to be 0.096 p. p. m. Results are given in Table VI.

TABLE VI. DOUBLE DISTILLATION  
(First 300 ml. by H<sub>2</sub>SO<sub>4</sub> at 160–165° C. Second 200 ml. by HClO<sub>4</sub> at 135–138° C. Standard titration: 0.15 mg. of F = 2.19 ml. net; 0.10 mg. of F = 1.47 ml. net.)

Sample No.	Added F Ml.	NaCl %	Net Titration Ml.	Net Titration minus Blank Ml.	Recovery %
10	0.15	0.07	2.39	2.07	94.5
11	0.15	0.07	2.40	2.08	95.0
12	0.15	0.07	2.43	2.11	96.3
13	0.15	0.07	2.49	2.17	99.1
14	0.10	0.07	1.59	1.27	86.4
15	0.10	0.07	1.62	1.30	88.4
16	0.10	0.07	1.51	1.19	81.0
17	0.10	0.07	1.43	1.11	75.5
18 <sup>a</sup>	0.00	0.07	0.18	..	..
19 <sup>b</sup>	0.00	0.07	0.32	..	..

<sup>a</sup> 1 gram of MgO only ashed.  
<sup>b</sup> 100 grams of tomatoes + 1 gram of MgO ashed.

The results show that the samples containing 0.15 mg. of added fluorine averaged about 96.2 per cent recovery. When 0.10 mg. of fluorine was involved the recoveries dropped inexplicably and became more erratic.

Summary

Suggestions have been made to facilitate the control of distillation of fluorine, and for the end point matching on the titration. Interfering ions are quantitatively compared.



The relative errors involved in the distillation of fluorine from ashed tomatoes by sulfuric acid and by perchloric acid are compared.

An efficient ashing procedure for the fluorine analysis of tomatoes using magnesium oxide is described.

A procedure which empirically gives an average recovery of 102.4 per cent, using a single perchloric acid distillation, is given.

### Acknowledgment

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## The Carotenoids in Forage

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FOR several years it has been known that vitamin A is an essential requirement for livestock. Since Steenbock (10) in 1919 reported a close correlation between yellow pigments and vitamin A, much attention has been directed towards a quantitative study of plant and animal pigments in relation to their vitamin A activity. Euler (2) limited the activity of yellow corn to the carotenes,  $C_{40}H_{56}$ . However, Kuhn and Grundman (5) isolated cryptoxanthin,  $C_{40}H_{56}O$ , which is also capable of serving as provitamin A. The zeaxanthin,  $C_{40}H_{56}O_2$ , a xanthophyll isolated chromatographically by Karrer (4), was found to be completely devoid of growth-promoting activity when fed to rats. Lutein, the xanthophyll found in alfalfa meal, is also without vitamin A activity.

The discovery of Borodin (1) in 1883 that the carotenoid pigments could be separated into alcohol-soluble and petroleum ether-soluble fractions has been the basis for most of the procedures that have been devised for the evaluation of carotene and other carotenoid pigments. As modern knowledge has shown that almost all the vitamin A potency of forage is due to its petroleum ether-phasic carotenoids, a rapid reliable spectrophotometric method for the estimation of these pigments would be a convenient index of its provitamin A content.

In 1913, Monteverde and Lumbimenko (6) reported a spectrophotometric method for the determination of the pigments

of green leaves, and in the same year Willstätter and Stoll (11) presented a procedure for the evaluation of carotene and xanthophyll which has served as a starting point for nearly all subsequent modifications. The latter method consists essentially of acetone-extraction of plant tissue, saponification of chlorophylls and esters, separation of the carotenoids by means of petroleum ether and aqueous methanol, and the colorimetric determination of the pigments. A petroleum ether solution of carotene or an aqueous standard solution of potassium dichromate served as a colorimetric standard.

In 1934, Guilbert (3) employed ethyl ether as an extraction solvent from which the pigments were transferred to petroleum ether. A standard solution of potassium dichromate (8) and Sprague's (9) dye standard were employed to evaluate the potency of carotene present.

In a recent paper Peterson, Hughes, and Freeman (7) reported a spectrophotometric method, which is a modification of the original Guilbert method, for the determination of carotene in forage. The main features of their method are as follows:

The sample (1 to 5 grams) is digested for 30 minutes with a saturated solution of potassium hydroxide in ethanol. Petroleum ether (b. p.  $40^{\circ}$  to  $60^{\circ}$  C.) is used as an extraction solvent, the chlorophyllins, flavones, alkali, and xanthophylls being removed by washing first with water and then with 85 and 90 per cent methanol, respectively. The petroleum ether solution, containing the carotene, is brought to volume and the carotene concentration is determined spectrophotometrically by recording the optical density measurements at wave lengths 4550, 4700, and 4800 Å. By proper calculations involving the extinction coefficient for pure  $\beta$ -carotene in petroleum ether, concentration, and optical density reading it is possible to evaluate the potency of carotene present.

Of the various methods of assaying carotene—biological, chemical, colorimetric, and spectrophotometric—the latter has in recent years been accepted as the most satisfactory (Morton, 1935, and other workers).

In the investigation of several methods in this laboratory before and after the publication of the modified Guilbert method, it appeared desirable to devise an extraction and evaluation method of equal or greater accuracy with a higher degree of precision and applicability.

Numerous experiments were made to ascertain the most satisfactory procedure for the extraction as well as the actual determination of the carotene potency of commercial samples of alfalfa meal. As a result, it was observed that the use of purified technical heptane as an extraction solvent was preferable to petroleum ether, ethyl ether, normal benzene, or pyridine. (The heptane was prepared by removing the un-

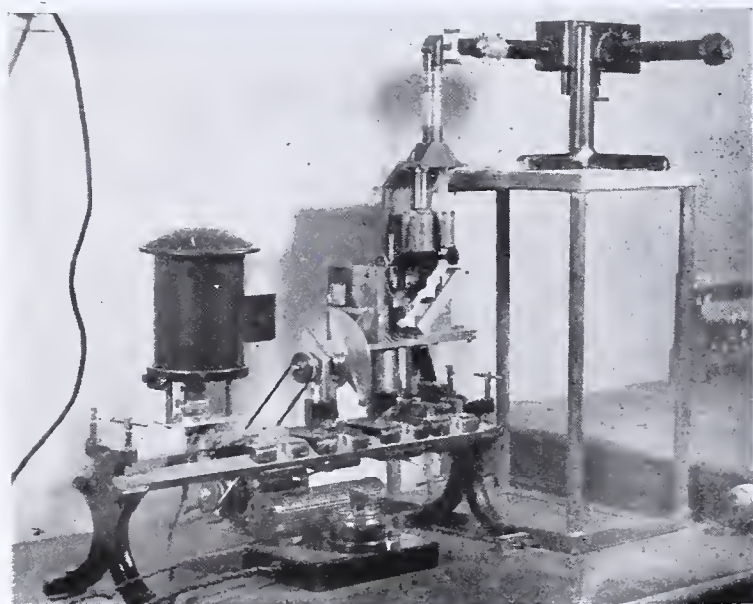


FIGURE 1. PHOTOGRAPH OF APPARATUS



saturated hydrocarbons and other impurities by agitating thoroughly with concentrated sulfuric acid, sp. gr. 1.83, removing the spent acid and mineral sulfonates formed, neutralizing the remaining acid with caustic soda, drying with calcium chloride, and then collecting the fraction which distilled between 94° and 98° C.) The extraction method has been further shortened, since the chlorophyllins, flavones, alkali, and xanthophylls can be removed directly from the heptane portion by washing repeatedly with 90 per cent methanol, as the mutual solubility of the two solvents is practically nil.

The instrument employed for these investigations was a modified Bausch & Lomb visual spectrophotometer, equipped with a Duboscq colorimeter arrangement and a rotating sector as shown in Figure 1. In the process of standardizing the instrument (slit width 150 to 175 microns) with pure  $\beta$ -carotene,<sup>1</sup> it was thought desirable to compare the results with those recorded with the medium-sized quartz Bausch & Lomb spectrophotometer. Experiments conducted on the absorption curves of pure  $\beta$ -carotene as well as on the unsaponifiable portions of alfalfa meal and yellow corn with the latter instrument showed maximum absorption bands at 4500 Å. The discrepancy between the two instruments when determined by comparing the  $E_{1\%}^{1\text{cm}}$  at 4500 Å. for pure  $\beta$ -carotene in heptane was within the limits of  $\pm 3$  per cent.

### Experimental Method

Weigh accurately into a 250-ml. digestion flask 5 grams (more or less, depending on the relative potency) of dehydrated alfalfa meal. Add 75 ml. of 10 per cent ethanolic potassium hydroxide and reflux on a hot plate or steam bath for 30 minutes. Agitate occasionally in order to facilitate digestion. Cool the contents of the flask, add 100 ml. of purified technical heptane, shake thoroughly, allowing the suspended material to settle, and decant the liquid portion into a 500-ml. separatory funnel. Re-extract the residue with 50-ml. portions of heptane until the resultant solution is colorless (three extractions are usually sufficient). Combine the heptane extracts and wash free from chlorophyllins, flavones, alkali, and xanthophylls by shaking thoroughly with 90 per cent methanol (five washes are generally sufficient), and re-extract the first methanol portion with 50 ml. of heptane. Examine the last washing for free alkali by testing a few milliliters with phenolphthalein. Distill the heptane portion to a small volume under a vacuum in the presence of nitrogen gas. The concentrated carotene solution is then made to volume (50 ml.) with heptane and is ready for examination in the visual spectrophotometer. The intensity of absorption at 4500 Å. is determined by taking the average of several readings.

To determine the percentage of carotene in the sample of alfalfa meal, the  $E_{1\%}^{1\text{cm}}$  4500 Å. (heptane) = 2380 (the extinction coefficient for pure  $\beta$ -carotene as determined by using the medium-sized quartz Bausch & Lomb spectrophotometer) is determined. By using the following equation it is possible to calculate the carotene for a 1 per cent solution:

$$(S \times F/R \times C) = \text{gamma of carotene for a 1\% solution}$$

where  
 $S$  = the screen factor  
 $F$  = the conversion factor for pure  $\beta$ -carotene in heptane  
 $R$  = the reading expressed in centimeters  
 $C$  = the concentration

The results can be conveniently expressed as gamma of carotene per gram of alfalfa meal.

The samples of dehydrated alfalfa meal used for this investigation were obtained from the Nopco Experiment Station, Flemington, N. J. Duplicate examinations were carried out on each sample. In order to compare the results obtained with the method as recommended by this laboratory, the

<sup>1</sup> S. M. A. Corporation, Cleveland Ohio, m. p. 184–184.5° C. corrected, optically inactive. On dissolving the  $\beta$ -carotene in chloroform and precipitating with methanol no change in melting point or absorption properties occurred.

samples were also prepared for examination by the modified Guilbert method as outlined by Peterson, Hughes, and Freeman (7).

Samples of dehydrated alfalfa meal when prepared for spectrophotometric examination by the modified Guilbert method and by the method as recommended by this laboratory compared favorably as to their carotene contents when examined in the visual spectrophotometer (Table I). The latter extraction method is considerably more rapid and requires less care in order to obtain a higher degree of precision. Objections to the former method are the difficulties encountered during the washings with water and 85 and 90 per cent methanol and the use of a petroleum ether of low boiling point as the extraction solvent.

TABLE I. CAROTENE CONTENT OF ALFALFA MEAL

Sample No.	Carotene by Modified Guilbert Method		Carotene by New Method		Differences between Deviations of Methods
	Deviation		Deviation		
	<i>Gamma per gram</i>		<i>Gamma per gram</i>		
A3R Alf. 3	72.1		73.9		
	71.4	0.7	73.6	0.3	+0.4
A3R Alf. 4	69.9		68.0		
	69.2	1.3	68.5	0.5	+0.8
A3R Alf. 8	67.3		69.0		
	68.9	1.6	69.6	0.6	+1.0
A3R Alf. 9	131.0		135.2		
	136.7	5.7	136.0	0.8	+4.9

The visual spectrophotometer is recommended as a convenient and rapid instrument for the quantitative evaluation of carotene. The results obtained with it are within  $\pm 3$  per cent of those recorded with the medium-sized quartz spectrophotometer. The main disadvantage of the visual spectrophotometer as compared to the medium-sized quartz spectrophotometer is that a permanent record is not recorded for each determination. With the quartz spectrophotometer a photographic absorption plate is taken for each sample and affords a satisfactory permanent record.

### Summary

A simple rapid spectrophotometric method is described for determining the carotene potency of alfalfa meal.

The results obtained on four samples of commercial dehydrated alfalfa meal with this method compare favorably with those obtained with the modified Guilbert method.

The visual spectrophotometer is described briefly and is recommended as an accurate, convenient instrument for routine evaluation of the carotene concentration of alfalfa meal.

A new absorption coefficient for pure  $\beta$ -carotene in heptane is reported.

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# Separation of Calcium as Sulfate by Precipitation in Concentrated Methanol Solution

## Application to the Analysis of Magnesite and Technical Magnesium Oxide

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Calcium can be quantitatively precipitated as sulfate in 90 per cent methanol solution. In contrast to sulfate separation methods which depend upon conversion of both calcium and magnesium to sulfates followed by extraction of the magnesium sulfate with a solvent, in the method here described the calcium sulfate is formed in solution without attempting to convert all or even most of the magnesium to sulfate. The precipitated calcium sulfate is readily ignited and weighed as the anhydrous salt.

AN ACCURATE, practical method for the direct separation and determination of small amounts of calcium in the presence of large amounts of magnesium is much needed. Though the oxalate method gives satisfactory results when the calcium-magnesium ratio is favorable, it gives poor results when magnesium is greatly preponderant, on account of the incomplete precipitation of calcium as oxalate. The critical studies of Stolberg (4), Kallauner and Preller (2), and Rodt and Kindscher (3) have shown that methods based upon the difference in the solubility of calcium sulfate and magnesium sulfate in ethanol solutions, which have frequently been described in the literature, are not very satisfactory. The principal sources of error are the noticeable solubility of calcium sulfate in solvents of low ethanol content and the slight solubility of magnesium sulfate in solutions in which the ethanol concentration is high enough to precipitate the calcium quantitatively. To obviate this fundamental difficulty Stolberg (4) proposed the use of a mixed solvent composed of ten parts of ethanol and ninety parts of methanol. Stolberg's method was investigated critically by Kallauner and Preller, who proposed an improvement in the method, and by Rodt and Kindscher. Satisfactory results can apparently be obtained by the modified Stolberg method, but from a practical standpoint the procedure requires too much time.

Willard and Smith (6) first suggested the use of methanol alone for the separation of calcium from magnesium as sulfate, precipitation to be made from perchlorate solution, but no systematic experiments were apparently carried out. According to the preliminary experiments of the present investigation, methanol is decidedly superior to ethanol for the separation of calcium from magnesium by the sulfate method and is also superior to other organic solvents completely miscible with water, such as acetic acid or acetone. By using a methanol-water solution of high alcohol concentration, the solubility of calcium sulfate can be reduced low enough to give quantitative results while at the same time the solubilities of many other salts, notably magnesium sulfate, are not reduced nearly so much as in ethanol-water solutions in which calcium sulfate is sufficiently insoluble for

By this method calcium can be accurately separated from a preponderant excess of magnesium and from small amounts of aluminum and iron, but not from other commonly associated elements such as strontium. The method is especially convenient for the rapid determination of calcium in magnesite and in technical grades of magnesium oxide. It is less satisfactory for the determination of high percentages of calcium, such as are found in limestone.

quantitative determination. As finally evolved, the sulfate separation method here recommended differs from most preceding ones in being a precipitation method in which calcium sulfate is caused to form in solution without attempting to convert all or even most of the magnesium to sulfate. In this respect it is essentially different from those methods which depend upon the evaporation of the calcium and magnesium solution with sulfuric acid to bring about the conversion of both elements to sulfate, with subsequent separation of the sulfates by extraction with a solvent.

### Methods of Precipitation Studied

The physical state of calcium sulfate precipitated in methanol solution is greatly influenced by the method of bringing the reacting solutions together. Though the order in which the reactants were mixed was found to have no effect on final completeness of precipitation, it had a decided influence on the time required for filtering and washing the precipitate (Table I).

TABLE I. EFFECT OF METHOD AND VOLUME ON TIME NEEDED FOR FILTRATION AND WASHING OF PRECIPITATE  
(Solution containing 100 mg. of calcium)

Method of Precipitation	Final Volume of Solution Ml.	Number of Trials	Average Time Min.
A <sup>a</sup>	100	3	10
	200	3	35
B <sup>b</sup>	100	3	70
	200	1	85
C <sup>c</sup>	100	2	40
	200	2	40
D <sup>d</sup>	100	2	80
	200	2	125

<sup>a</sup> Calcium solution + dilute sulfuric acid + methanol.

<sup>b</sup> Calcium solution + methanol + dilute sulfuric acid.

<sup>c</sup> Calcium solution + mixture of dilute sulfuric acid and methanol.

<sup>d</sup> Methanol + mixture of calcium solution and dilute sulfuric acid.

The final concentration of methanol in these experiments was 90 per cent, and a fixed amount of dilute sulfuric acid was used. The most favorable conditions are provided by method A. A modification of this method, to include slow evaporation of the calcium solution containing sulfuric acid to small volume before addition of the methanol, was found advantageous in reducing the time needed for filtering and washing large amounts of calcium sulfate, since the major part

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of the calcium is precipitated in large crystals before the addition of the nonaqueous solvent.

### General Procedure Adopted

The calcium is precipitated by one of the two following methods from a neutral chloride, nitrate, or perchlorate solution that is free from ammonium salts, barium, strontium, and lead, but may contain in addition to calcium and magnesium, small amounts of aluminum, iron, and manganese, and very small amounts of the alkalis.

I. Evaporate the solution to a volume of 4.5, 9.0, or 19 ml. or evaporate to dryness and dissolve in sufficient water to obtain the desired volume. Then add 0.5 or 1.0 ml. of 9 *N* sulfuric acid (1 volume of concentrated acid to 3 volumes of water) and precipitate the calcium sulfate by the slow addition of 45, 90, or 180 ml. of methanol in accordance with the volume of the aqueous solution, so that the final volume is 50, 100, or 200 ml. having a methanol concentration of 90 per cent. Stir constantly during addition of the methanol.

II. Add 1.0 or 2.0 ml. of 9 *N* sulfuric acid to the sample solution and evaporate until the volume is 5.0 ml. Then add 15 ml. of water and precipitate the calcium by the slow addition of 180 ml. of methanol while stirring constantly.

After precipitating by either method and allowing the solution to stand until precipitation is complete, filter through a weighed porcelain filter crucible, preferably a type A1 Koenig crucible. Wash the precipitate with 90 per cent methanol, first by decantation, then by stirring up the precipitate collected in the filter crucible with a stream of wash liquid and allowing the precipitate to remain in contact with each portion of wash liquid for a few minutes. Depending upon the quantity of calcium and other metals that are present, a total of 30 to 100 ml. will be required for washing. Dry the crucible and its contents for 30 to 45 minutes at 110° C., then ignite in an electric muffle for 30 to 45 minutes at 400° to 450° C., cool in a desiccator, and weigh as anhydrous calcium sulfate.

The choice of the method of precipitation is governed largely by the amount of calcium to be precipitated. With 5 mg. or less, method I and a total volume of 50 ml. should be used. With more than 5 but somewhat less than 100 mg., method I should be used with a total volume of 100 ml. When the quantity of calcium is about 100 mg. and foreign ions are present in low concentration, method I should be used with a total volume of 100 or 200 ml. On the other hand, when the amount of calcium is around 100 mg. and the concentration of foreign ions is high, or when the amount of calcium is considerably more than 100 mg., method II should be used. It is necessary to use a large volume of solution when the amount of calcium is high because calcium sulfate precipitated in methanol solution is very voluminous.

TABLE II. EFFECT OF COMPOSITION OF MEDIUM ON COMPLETENESS OF PRECIPITATION BY SULFURIC ACID IN METHANOL SOLUTION

CH <sub>3</sub> OH % by volume	Total Volume of Solution Ml.	Ca Taken Gram	Ca Found Gram	Difference Error Gram
70	50	0.0010	0.0005	-0.0005
80	50	0.0010	0.0010	±0.0000
90	50	0.0010	0.0010	±0.0000
70	100	0.0010	0.0000	-0.0010
80	100	0.0010	0.0008	-0.0002
90	100	0.0010	0.0010	±0.0000
70	100	0.1004	0.0988	-0.0016
80	100	0.1007	0.1003	-0.0004
90	100	0.1021	0.1018	-0.0003

The methanol should contain at least 99 per cent of the alcohol, but the most expensive grade of absolute methanol need not be used in this method.

The time of standing after precipitation is governed largely by the amounts of calcium and magnesium present, and by the total volume of solution used (see tables).

It is not possible to obtain quantitative results by weighing the precipitate in the air-dried state or after drying

at 110°, since calcium sulfate precipitated in 90 per cent methanol solution is apparently an indefinite mixture of the dihydrate and hemihydrate. However, when ignited at the proper temperature it becomes inert anhydrous calcium sulfate that can be weighed without difficulty.

### Conditions for Quantitative Precipitation

Complete precipitation of calcium as sulfate in methanol solution occurs only when the methanol concentration reaches about 90 per cent, as is shown by Table II. Except for changing the composition of the medium, these results were obtained by method I. In practice it is not desirable to precipitate the calcium in a solution containing more than 90 per cent methanol because aqueous sample and reagent solutions of inconveniently small volume are then required.

TABLE III. EFFECT OF TIME OF STANDING ON COMPLETENESS OF PRECIPITATION OF CALCIUM AS SULFATE

(In 90 per cent methanol solution)				
Time of Standing Min.	Mg Present Gram	Ca Taken Gram	Ca Found Gram	Difference Error Gram
30	None	0.0010	0.0010	±0.0000
30	None	0.0010	0.0010	±0.0000
60	None	0.0010	0.0010	±0.0000
60	None	0.0010	0.0010	±0.0000
15	None	0.0100	0.0100	±0.0000
30	None	0.0100	0.0099	-0.0001
60	None	0.0100	0.0101	+0.0001
90	None	0.0100	0.0099	-0.0001
30	0.0100	0.0010	0.0009	-0.0001
30	0.0250	0.0010	0.0009	-0.0001
30	0.0500	0.0010	0.0004	-0.0006
60	0.0500	0.0010	0.0006	-0.0004
120	0.0500	0.0010	0.0009	-0.0001
30	0.1000	0.0010	0.0003	-0.0007
180	0.1000	0.0010	0.0007	-0.0003
240	0.1000	0.0010	0.0008	-0.0002
60	0.1000	0.0010	0.0009	-0.0001 <sup>a</sup>
120	0.1000	0.0010	0.0009	-0.0001 <sup>a</sup>
180	0.1000	0.0010	0.0010	±0.0000 <sup>a</sup>
240	0.1000	0.0010	0.0010	±0.0000 <sup>a</sup>

<sup>a</sup> Precipitation made in a total volume of 50 ml. in these cases, the other precipitations being made in a volume of 100 ml.

At least twice the equivalent amount of sulfuric acid should be employed, and precipitation of calcium as sulfate is still quantitative when a very considerable excess of reagent is present—for example, precipitation of only 10 mg. of calcium in a 100-ml. volume was found to be complete when as much as 1 ml. of 96 per cent sulfuric acid was used. This amount of reagent is sufficient for any amount of calcium that can be conveniently handled by this method. However, a large excess of sulfuric acid should be avoided in the presence of ions other than calcium and magnesium, since sulfates insoluble in 90 per cent methanol may be coprecipitated with the calcium sulfate. Because of their tendency to increase the solubility of calcium sulfate, acids other than sulfuric cannot be present except in very low concentration.

When calcium is present alone precipitation is complete after a short period of standing, as is shown by the first set of results in Table III. It is necessary to wait more than an hour for complete precipitation only if the quantity of calcium amounts to but a few tenths of a milligram. On the other hand, as shown by the second set of results, when considerable magnesium is also present a much longer time is needed for the complete precipitation of small amounts of calcium. The effect of magnesium in retarding the quantitative precipitation of calcium sulfate is much less marked when large amounts of calcium are precipitated. It is desirable to restrict the total volume of solution as much as possible in order to obtain a more rapid quantitative precipitation of small amounts of calcium, especially when a large excess of magnesium is present. This is readily seen by comparing the last four results in Table III with the three preceding ones.



### Test Analyses on Solutions

For the analytical experiments on pure calcium solutions and on solutions containing calcium and other metal ions, a highly purified sample of calcium carbonate, prepared by the reprecipitation of a reagent-grade salt, was used as the standard of reference. Standard solutions were prepared by dissolving accurately weighed quantities of this calcium carbonate in the necessary quantity of hydrochloric acid and diluting to definite volumes in calibrated flasks. The concentration of each solution in respect to calcium was checked by evaporating definite volumes with a slight excess of sulfuric acid in a platinum dish and weighing the residual calcium sulfate. The standard magnesium solutions were prepared from distilled metallic magnesium of high purity, and the standard solutions of the other metals were made from pure salts. Samples for the test analyses were prepared from accurately measured volumes of these standard solutions.

TABLE IV. DETERMINATIONS OF SMALL AMOUNTS OF CALCIUM IN PURE CALCIUM CHLORIDE SOLUTIONS

Final Volume of Solution Ml.	Time of Standing Min.	Ca Taken Gram	Ca Found Gram	Difference Error Gram
50	60	0.0001	0.0000	-0.0001
50	240	0.0001	0.0001	±0.0000
50	60	0.0003	0.0002	-0.0001
50	240	0.0003	0.0002	-0.0001
50	60	0.0005	0.0005	±0.0000
50	240	0.0005	0.0005	±0.0000
100	30	0.0010	0.0010	±0.0000
100	30	0.0010	0.0010	±0.0000
100	60	0.0010	0.0010	±0.0000
100	60	0.0010	0.0010	±0.0000
100	30	0.0050	0.0050	±0.0000
100	30	0.0100	0.0099	-0.0001
100	30	0.0100	0.0100	±0.0000
100	60	0.0100	0.0098	-0.0002
100	90	0.0100	0.0099	-0.0001
200	30	0.0100	0.0099	-0.0001
200	30	0.0100	0.0099	-0.0001

As will be seen from Table IV, no difficulty was experienced in making accurate determinations of small amounts of calcium in the absence of other metal ions.

In Table V are shown results obtained on trial determinations of large amounts of calcium in pure calcium chloride solutions.

TABLE V. DETERMINATION OF LARGE AMOUNTS OF CALCIUM (Lack of quantitative precipitation above a certain limit)

Method of Precipitation	Final Volume of Solution Ml.	Time of Standing Min.	Ca Taken Gram	Ca Found Gram	Difference Error Gram
I	100	30	0.1000	0.1001	+0.0001
I	100	30	0.1000	0.1001	+0.0001
I	100	60	0.1000	0.0999	-0.0001
I	100	60	0.1000	0.1000	±0.0000
I	200	30	0.0998	0.0998	±0.0000
I	200	30	0.1000	0.0998	-0.0002
I	200	60	0.1000	0.1000	±0.0000
II	200	30	0.0998	0.0997	-0.0001
II	200	45	0.0998	0.0996	-0.0002
I	200	45	0.1503	0.1500	-0.0003
I	200	75	0.1513	0.1509	-0.0004
I	100	30	0.2000	0.1994	-0.0006
I	200	30	0.2000	0.1991	-0.0009
I	200	60	0.2009	0.2004	-0.0005
II	200	30	0.2008	0.2005	-0.0003
II	200	30	0.2007	0.1996	-0.0011
II	200	60	0.1997	0.1984	-0.0013
I	200	45	0.3008	0.2992	-0.0016
I	200	75	0.2998	0.2982	-0.0016
II	200	30	0.3017	0.3006	-0.0011
II	200	60	0.4005	0.3986	-0.0019

Regardless of how the general procedure was applied, precipitation was incomplete above a certain limit, the results being often poor with 200 mg. of calcium and invariably so with as much as 300 or 400 mg. In part, at least, these low results can be ascribed to the solvent effect on the calcium sulfate of the ions remaining in solution after precipitation. Various attempts were made to eliminate this source of

error—for example, precipitations were tried in acetate or perchlorate solutions in order to avoid the effect of chlorid ion. The effect of greatly reducing the hydrogen-ion concentration was also tried, precipitation being made with alkyl ammonium sulfates instead of with sulfuric acid. Satisfactory results could not be obtained by any of these variations of the general method. However, the fact that precipitation is incomplete when the amount of calcium reaches about 200 mg. does not mean that this method cannot be applied in practice to the determination of moderate or even high percentages of calcium, since the whole difficulty can be avoided by properly restricting the weight of the original sample.

TABLE VI. DETERMINATION OF SMALL AMOUNTS OF CALCIUM IN THE PRESENCE OF A LARGE PROPORTION OF MAGNESIUM

Final Volume of Solution Ml.	Time of Standing Hours	Mg Present Gram	Ca Taken Gram	Ca Found Gram	Difference Error Gram
50	4	0.1000	0.0005	0.0000	-0.0005
50	8	0.1000	0.0005	0.0002	-0.0003
50	24	0.1000	0.0005	0.0005	±0.0000
50	1	0.1000	0.0010	0.0009	-0.0001
50	2	0.1000	0.0010	0.0009	-0.0001
50	3	0.1000	0.0010	0.0010	±0.0000
50	4	0.1000	0.0010	0.0010	±0.0000
50	9.5	0.2000	0.0010	0.0008	-0.0002
50	9.5	0.3000	0.0010	0.0005	-0.0005
50	9.5	0.4000	0.0010	0.0002	-0.0008
50	9.5	0.5000	0.0010	0.0002	-0.0008
50	24	0.5000	0.0010	0.0005	-0.0005
50	1	0.1000	0.0050	0.0050	±0.0000
50	2	0.1000	0.0050	0.0047	-0.0003
50	4	0.1000	0.0050	0.0053	+0.0003
50	4	0.2000	0.0050	0.0051	+0.0001
100	0.5	0.2000	0.0050	0.0048	-0.0002
100	0.5	0.3000	0.0050	0.0046	-0.0004
100	1	0.3000	0.0050	0.0047	-0.0003
50	1	0.1000	0.0100	0.0100	±0.0000
50	2	0.1000	0.0100	0.0100	±0.0000
50	4	0.1000	0.0100	0.0102	+0.0002
50	4	0.2000	0.0100	0.0103	+0.0003
100	0.5	0.1000	0.0100	0.0100	±0.0000
100	0.5	0.1000	0.0100	0.0098	-0.0002
100	0.5	0.1000	0.0100	0.0099	-0.0001
100	0.5	0.5000	0.0100	0.0097	-0.0003

The effect of a preponderant excess of magnesium on the quantitative precipitation of calcium is shown by Table VI. It is evident that complete precipitation of the calcium when the proportion of magnesium to calcium is as high as 200 to 1 takes place only after an inconveniently long period of standing, and that when the proportion is higher than this it is not possible to obtain quantitative results. On the other hand, when the proportion is 100 to 1, or less, precipitation of the calcium is complete after a conveniently short period of standing. In blank experiments in which 200 to 500 mg. of magnesium as chloride and 0.5 ml. of 9 N sulfuric acid were present in 50 ml. of 90 per cent methanol, no precipitation took place even after several hours' standing.

That no difficulty was experienced in the determination of large amounts of calcium in the presence of like amounts of magnesium is illustrated by Table VII. The results of experiments in which the magnesium was actually determined in the filtrate after the calcium determination are shown in Table VIII. In these experiments the calcium filtrates were evaporated to dryness on the steam bath, and, after dissolving the residues, the magnesium was precipitated as oxalate in 85 per cent acetic acid solution and weighed as oxide according to the method of Elving and Caley (1). The accuracy of this scheme of separation and determination can be judged from the results.

Small amounts of aluminum, iron, or manganese, in the form of salts soluble in 90 per cent methanol, do not interfere with the quantitative precipitation of calcium by this method. That no precipitation with sulfuric acid takes place when limited quantities of such salts are present alone was shown by appropriate blank experiments. For example, no



TABLE VII. DETERMINATION OF A LARGE AMOUNT OF CALCIUM IN THE PRESENCE OF AN EQUAL WEIGHT OF MAGNESIUM

Method of Pre- cipitation	Final Volume of Solution Ml.	Mg Present Gram	Ca Taken Gram	Ca Found Gram	Difference Error Gram
I	100	0.1000	0.1000	0.1002	+0.0002
I	100	0.1000	0.1000	0.1000	±0.0000
I	100	0.1000	0.1000	0.1002	+0.0002
I	100	0.1000	0.1000	0.0999	-0.0001
I	100	0.1000	0.1000	0.1001	+0.0001
II	200	0.1000	0.0998	0.0994	-0.0004
II	200	0.1000	0.0998	0.0995	-0.0003

TABLE VIII. DETERMINATION OF CALCIUM AND MAGNESIUM IN THE SAME SOLUTION

Ca Taken Gram	Ca Found Gram	Difference Error Gram	Mg Taken Gram	Mg Found Gram	Difference Error Gram
0.0100	0.0099	-0.0001	0.0101	0.0102	+0.0001
0.0100	0.0099	-0.0001	0.0101	0.0103	+0.0002
0.0100	0.0100	±0.0000	0.0102	0.0998	-0.0004
0.0100	0.0098	-0.0002	0.1002	0.1005	+0.0003
0.1000	0.0999	-0.0001	0.0101	0.0104	+0.0003
0.1000	0.1001	+0.0001	0.0101	0.0104	+0.0003
0.1000	0.1002	+0.0002	0.1002	0.1002	±0.0000
0.1000	0.1000	±0.0000	0.1002	0.1002	±0.0000

recipitation took place even after 48 hours' standing with 0 mg. of aluminum, manganese, or iron as chlorides in 10 ml. of 90 per cent methanol containing several drops of sulfuric acid. In analogous experiments with sodium and lithium chlorides the solutions remained clear as long as 7 hours. On the other hand, in similar experiments in which potassium was present as chloride, immediate precipitation resulted when the solution contained more than 4 mg. of potassium. With 2.5 mg. of potassium, precipitation began after 2 hours, but with 2 mg. of potassium no precipitation was observed.

In Table IX are shown results of quantitative experiments in which calcium was precipitated and determined in the presence of known amounts of individual foreign cations. Sodium and potassium interfere seriously, the interference of potassium being very marked, especially when the first method of precipitation is used. Fortunately, in the practical situations where this method is most applicable, as in the analysis of magnesite, the amount of acid-soluble sodium or potassium in a sample of moderate size is usually so small that no interference will result. When a large amount of soluble potassium is present in a sample, it is possible to avoid the difficulty by dissolving the sample in perchloric acid, removing the excess of perchloric acid, and extracting the residue with successive small portions of 90 per cent methanol. The calcium can then be precipitated from the combined extracts by means of sulfuric acid. Ammonium, like potassium, interferes seriously in this method because of the low solubility of its sulfate in methanol solution. Ammonium salts must therefore be removed. The usual nitric acid oxidation method is suitable, though all free nitric acid must be volatilized from the residual salts before proceeding to the determination of the calcium. That no interference results from the presence of lithium is illustrated by Table IX.

TABLE IX. PRECIPITATION OF CALCIUM IN THE PRESENCE OF VARIOUS METALS

Method of Pre- cipitation	Solution Volume Ml.	Metal Present Gram	Ca Taken Gram	Ca Found Gram	Difference Error Gram
I	100	0.0500 Al	0.0100	0.0100	±0.0000
I	100	0.1000 Al	0.0100	0.0098	-0.0002
II	200	0.0100 Al	0.0998	0.0998	±0.0000
I	100	0.0100 Fe	0.0100	0.0100	±0.0000
I	100	0.1000 Fe	0.0100	0.0102	+0.0002
II	200	0.0250 Fe	0.0998	0.1000	+0.0002
II	200	0.0500 Fe	0.0998	0.0993	-0.0005
I	100	0.1000 Li	0.0100	0.0102	+0.0002
II	200	0.1000 Li	0.0998	0.0998	±0.0000
I	100	0.0050 Na	0.0100	0.0110	+0.0010
I	200	0.0050 Na	0.0100	0.0108	+0.0008
II	200	0.0050 Na	0.0998	0.1005	+0.0007
II	200	0.0100 Na	0.0998	0.1005	+0.0007
I	100	0.0050 K	0.0100	0.0112	+0.0012
I	200	0.0100 K	0.0100	0.0120	+0.0020
II	200	0.0050 K	0.0998	0.1000	+0.0002
II	200	0.0100 K	0.0998	0.1004	+0.0006

A rather satisfactory separation of calcium as sulfate can be made in the presence of small or moderate amounts of aluminum or iron. However, when the aluminum or iron is high amount, incomplete precipitation of the calcium results. Prior removal of these elements by the usual methods is then

necessary. If iron is present in excessive amount and the sample has been dissolved in perchloric acid, it is possible to eliminate most or all of the iron rapidly by evaporating the solution of the sample to dryness on the hot plate and heating the residue near the boiling point of perchloric acid until the free perchloric acid is removed. The iron perchlorate is decomposed and an insoluble residue of iron oxide remains behind, whereas calcium perchlorate remains undecomposed and may be dissolved out quantitatively from the residue.

TABLE X. DETERMINATION OF CALCIUM IN SYNTHETIC MIXTURES

	Sample A	Sample B	Sample C	Sample D
Al present, gram	0.0100	0.0100	0.0300	0.0300
Fe present, gram	0.0100	0.0100	0.0200	0.0200
Mg present, gram	0.1000	0.1000	0.0100	0.0100
Na present, gram	0.0020	0.0020	0.0050	0.0050
K present, gram	0.0020	0.0020	0.0050	0.0050
Ca present, gram	0.0998	0.0998	0.0998	0.0998
Ca found, gram	0.0999	0.0999	0.1001	0.1001
Difference, error, gram	+0.0001	+0.0001	+0.0003	+0.0003

The validity of this method of separation was demonstrated by suitable experiments. For example, two solutions, one containing 0.0199 gram of calcium and 0.050 gram of iron, the other containing 0.0199 gram of calcium and 0.100 gram of iron, were evaporated with perchloric acid, and after baking the residue, cooling, and treating with water, the insoluble iron oxide residues were filtered off with the aid of filter pulp and washed with water. On determining calcium in the filtrates, the calcium sulfate precipitates weighed 0.0674 and 0.0677 gram, respectively, as compared to the calculated 0.0677 gram. These calcium sulfate precipitates were dissolved and tested for iron by means of cupferron, but less than 0.05 mg. of iron was found in each case. On dissolving the iron residues and testing for calcium by means of picrolonic acid, no calcium could be detected. For the removal of interfering barium, strontium, or lead the nitric acid method of Willard and Goodspeed (5) is the most suitable to use in connection with this method for the determination of calcium.

In Table X are shown results obtained on synthetic samples in which various foreign ions were present in about the same proportions as in solutions of analytical samples of either limestone or dolomite. The second method of precipitation was used on all four samples, and the time allowed for precipitation was 35 minutes. The method is satisfactory for the direct determination of calcium in complex samples of this kind.

### Test Analyses on Complex Materials

This method was further tested by applying it to mineral or rock samples of accurately known composition. The method seems to be especially satisfactory for the rapid determination of low percentages of calcium in complex materials that contain a high percentage of magnesium, low or moderate percentages of aluminum or iron, and very low percentages of potassium or sodium, such as, for example, natural or burned magnesite. In Table XI are shown the results ob-



tained on the Bureau of Standards sample of burned magnesite (standard sample 104).

After a preliminary ignition in platinum, the weighed samples of this material were dissolved in a mixture of about 10 ml. of water and 10 ml. of 60 per cent perchloric acid in porcelain casseroles. The solutions were then evaporated nearly to dryness, and the covered casseroles were heated on the sand bath for 20 minutes at a temperature at which copious fumes of perchloric acid were evolved. After cooling, the residues were treated with water and the silica was filtered off and washed in the customary way. In the case of the first two samples in Table XI the iron was eliminated by evaporating the silica filtrates to dryness and decomposing the iron perchlorate, as described above; in the other samples the iron and accompanying elements were removed by precipitation with ammonia in dilute solution, the ammonium salts in the resulting filtrates being eliminated by evaporation with nitric acid. In all samples the calcium was precipitated by method I of the general procedure, the volumes of the solutions and the times of standing being varied as shown.

TABLE XI. DETERMINATION OF CALCIUM IN STANDARD BURNED MAGNESITE SAMPLE

Sample Taken Gram	Volume of Solution Ml.	Time of Standing Hours	CaO Found %
1.2279	100	1	3.32
0.9876	200	6.5	3.33
0.9661	100	1	3.39
1.1830	100	1	3.35
0.9861	200	1	3.31
1.2122	200	1	3.30
1.2684	100	2	3.30
1.3995	200	2	3.35
			Av. 3.33
			3.35

Stated average, Bureau of Standards certificate

Both the individual results and the average agree well with the established percentage. Either method for the removal of the iron leads to the same results. Attempts to determine the calcium in this particular sample without prior removal of the iron did not yield satisfactory results by reason of the relatively high proportion of iron (7.07 per cent). However, when the percentage of iron is not quite so high good results can be obtained either without removing the iron or by removing most of it at the same time that the silica is eliminated. This was shown by a series of analyses, made in collaboration with another laboratory, of samples of technical magnesium oxide, both powdered and coarsely crystalline. The procedure finally developed for the determination of calcium in such materials is, because of its brevity and demonstrated usefulness, given here in detail.

To a 1,000-gram sample in a 250-ml. Pyrex beaker add 5 ml. of water and 10 ml. of 60 per cent perchloric acid, and then heat on the steam bath until solution is complete or only a small residue of silica remains. Fume off the excess of perchloric acid by placing the beaker on a high-temperature hot plate. If necessary remove the last traces of perchloric acid by heating the beaker wall with a flame. After cooling, dissolve the salts in about 20 ml. of water. Filter off the silica and wash with successive small portions of hot water. To save time in evaporation, the total volume of wash water should not exceed about 50 ml.

Catch the filtrate and washings in a 250-ml. beaker and evaporate to a volume of 9 ml. Then add 1 ml. of 9 N sulfuric acid and precipitate the calcium by adding very slowly from a pipet 90 ml. of methanol while stirring constantly. After allowing the mixture to stand at least 1 hour (several hours if the precipitate is small) filter off the calcium sulfate on a weighed porcelain filter crucible. Wash with successive small portions of 90 per cent methanol, using a total of about 50 ml. Dry and weigh the calcium sulfate as directed under the general procedure.

This procedure is not satisfactory when the iron in the sample exceeds about 3 per cent or the total potassium and sodium about 0.5 per cent. Accurate results for the calcium are not obtained when less than 0.5 per cent is present.

Some comparative results on commercial samples, obtained independently by different operators, are shown in Table XII. The results obtained by method B, considered more or less standard on such material, correspond well with the results obtained in this laboratory by the methanol procedure. However, because it does not involve several separations and extended manipulation the latter procedure is probably more accurate in practice, and has the decided advantage of being much shorter.

TABLE XII. DETERMINATIONS OF CALCIUM OXIDE IN SAMPLES OF TECHNICAL MAGNESIUM OXIDE

Method and Laboratory	Sample I, %	Sample II, %	Sample III, %
A <sup>a</sup>	0.80	2.32	0.90
B <sup>b</sup>	0.82	2.25	0.91
C <sup>c</sup>	..	2.10	0.82

<sup>a</sup> Methanol precipitation procedure.

<sup>b</sup> A tedious but apparently accurate method that involved first converting the metals to sulfates and removing the major part of the magnesium sulfate by extraction with ethanol. After dissolving the residual salts, aluminum and iron were removed by ammonia precipitation, and calcium was determined in the filtrate by double precipitation as oxalate.

<sup>c</sup> After removing silica, aluminum, and iron by conventional methods, calcium and magnesium were precipitated together as phosphates. Then the mixed precipitate was dissolved in dilute sulfuric acid and calcium was precipitated as sulfate by addition of ethanol. This precipitate was dissolved and calcium was finally determined by the oxalate method.

Results obtained on the Bureau of Standards argillaceous limestone sample (standard sample 1a) and on the Bureau of Standards dolomite sample (standard sample 88) are shown in Table XIII. In these analyses silica was removed by means of perchloric acid, and the excess perchloric acid was eliminated by volatilization. Because of the small amounts present no attempt was made to remove the iron or aluminum, the filtrates from the silica separation being used directly for the preparation of the solution for the calcium determination. The calcium was precipitated in each sample by method II, the time of standing being varied as shown. That the results on the argillaceous limestone sample are as near as they are to the stated value is due in part to the fact that the strontium oxide in the sample (0.12 per cent) is here counted with the calcium oxide. A deduction of 0.09 per cent from each individual result and from the average should be made to give the percentages due to calcium alone. If this is done the results on the two samples deviate to about the same extent from the stated value, both being a trifle on the low side. On the whole, however, determinations of calcium in carbonate rock by this method are accurate enough for most purposes, and probably as good as those often obtained in practice by the oxalate method.

TABLE XIII. DETERMINATION OF CALCIUM IN STANDARD CARBONATE ROCK SAMPLES

Standard Sample	Sample Taken for Analysis	Time of Standing	CaO Found
	<i>Gram</i>	<i>Hours</i>	<i>%</i>
Argillaceous limestone	0.5985	0.5	41.23
	0.5397	0.5	41.28
	0.7182	1.0	41.25
	0.5140	1.0	41.28
			Av. 41.26
Stated average, Bureau of Standards certificate			41.32
Dolomite	0.9334	0.5	30.35
	0.6126	0.5	30.35
	0.8447	1.0	30.28
	0.4445	1.0	30.45
			Av. 30.36
Stated average, Bureau of Standards certificate			30.49

In the course of continuous experimentation with this method over a period of many months no unpleasant physiological effects resulted from working with methanol. Since the solvent contains 10 per cent of water, there appears to be no explosion hazard involved in evaporating filtrates from calcium determinations to dryness in cases where magnesium



and alkali metals are in the form of perchlorates from treatment of the original sample with perchloric acid.

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# Estimation of Ascorbic Acid in Citrus Juices

## An Iodine Titration Method

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THIS iodine titration method for estimation of ascorbic acid was first described before the Food and Nutrition Section of the American Public Health Association in Pasadena, Calif., September 6, 1934, in a paper by A. J. Lorenz, W. Reynolds, and J. W. Stevens. Since that time the method has had extensive and satisfactory use by the California Fruit Growers Exchange in the estimation of the ascorbic acid content of citrus juices and various citrus juice products. It also has been used by Mack, Fellers, MacLinn, and Dean (12), and Roberts (16) in studies on citrus beverages and juices.

In the chemical estimation of ascorbic acid (vitamin C) in various biological materials the two reagents most commonly employed are 2,6-dichlorophenolindophenol and iodine. Titrations with the former reagent are made either in slightly acid solution as originally recommended by Tillmans, Hirsch, and Hirsch (19), or in relatively strong acid solution as described by Birch, Harris, and Ray (2). The iodine titration is restricted to use in relatively strong acid solution.

An important consideration in the chemical estimation of ascorbic acid is the specificity of the reagent employed. Many natural materials contain in addition to ascorbic acid various reducing substances such as glutathione and certain phenolic compounds which may titrate along with the vitamin. Since iodine is a strong oxidizing agent it may react with these interfering substances and hence the results obtained with the reagent may not be specific for vitamin C. The 2,6-dichlorophenolindophenol, on the other hand, is a relatively weak oxidizing agent and thus does not react so readily with these nonvitamin reducing substances. Because of the greater specificity of this reagent for vitamin C, many workers have preferred it to iodine.

Although the specificity of the method is of vital concern, certain other factors are important: standardization of the reagents employed, stability of the reagents, ease and rapidity of the titration procedure, sharpness of the end point, accuracy or reproducibility of the results, and, for extensive routine testing, the cost of the reagents.

The iodine method has certain advantages and except for lack of specificity for vitamin C and the indefinite end point it would undoubtedly be used to a greater extent. Careful study of the various factors involved have shown that the most serious objections to its use may be largely eliminated. The interference of nonvitamin reducing substances may be lessened and the end point improved by proper adjustment of the acidity of the titration mixture by the addition of a strong mineral acid as disclosed by Tillmans, Hirsch, and Hirsch (2). The end point may be improved further by the use of a double back-titration, which gives better results than the back-titration employed by Tillmans and his associates. The

following procedure was adopted for obtaining these improvements in the iodine method for citrus juices.

### Method

Twenty milliliters of the natural-strength juice are transferred to a 250-ml. Erlenmeyer flask and 4 ml. of 12 *N* sulfuric acid are added. The added acid lowers the pH of the sample to about 0.02 to 0.08 by the hydrogen electrode. Freshly standardized 0.01 *N* iodine solution is then added until an excess of 1 or 2 ml. is present. Excess iodine may be detected by color change in the sample or by the addition of a drop of starch solution. The test solution is allowed to stand for about 0.5 minute for the reaction to go to completion. Standardized 0.01 *N* thiosulfate solution is now added to give an excess of about 1 ml., with 3 ml. of 0.5 per cent starch solution added as the indicator. A trial titration may be run to determine the amounts of iodine and thiosulfate solutions needed to obtain the desired excess values. Finally, more of the 0.01 *N* iodine solution is added slowly until the well-known starch-iodine end point is reached. The total volume of the iodine solution added minus the volume of thiosulfate solution used (on the iodine equivalent basis) equals the volume of iodine solution consumed by the reducing substances in the sample. One milliliter of 0.01 *N* iodine solution is equivalent to 0.88 mg. of ascorbic acid.

### Preparation and Standardization of Reagents

**IODINE SOLUTION.** An approximately 0.1 *N* stock solution is prepared by dissolving 25 grams of potassium iodide in as little distilled water as possible and then adding about 12.7 grams of resublimed iodine. After the iodine has dissolved, the solution is diluted to 1 liter with distilled water. The solution is protected from light by storing in a dark or wrapped bottle. From this stock solution the 0.01 *N* solution is prepared as needed for use in the ascorbic acid titration by diluting about 100 ml., together with 22.5 grams of potassium iodide, to 1 liter.

The normality of the dilute solution is checked, at the time of use, by titration of 20- or 25-ml. portions with standardized 0.01 *N* thiosulfate solutions, using starch solution as the indicator. The starch solution, about 3 ml., is not added until the titration is almost complete.

**STARCH SOLUTION.** The 0.5 per cent starch solution is prepared according to the procedure outlined by Treadwell and Hall (20). Five grams of powdered potato starch are triturated into a paste with a little water and poured slowly into a liter of boiling distilled water. Boiling is continued 1 or 2 minutes to obtain a nearly clear solution. The solution is cooled and allowed to stand several hours and is then filtered and transferred to 50-ml. bottles. After heating for about 2 hours in a steamer, or water bath, the bottles are closed with cork stoppers that have been dipped in hot paraffin. Starch solution prepared in this manner will give a good color reaction and retain its sensitivity for several months and is preferred to most of the soluble starch preparations. The solution may lose its sensitivity within a few days after the bottle is opened, usually because of mold growth.

**THIOSULFATE SOLUTION.** The convenience of the iodine titration method depends to a considerable extent upon the stability of the thiosulfate solution used as the standardizing agent, and consequently particular attention should be given to its preparation.



The deterioration of thiosulfate solutions has been attributed to a number of causes and several methods have been advanced for stabilizing the reagent. Kolthoff (8), Mayr (13), Schulek (17), Winkler (21), Hahn and Clos (5), Kolliker (7), and others are of the opinion that the deterioration of the reagent is due largely to the action of certain types of bacteria. Hahn and Windisch (6), Mayr and Kerschbaum (14), and Law (9) have pointed out the significance of carbon dioxide in the deterioration processes. Traces of copper may catalyze the decomposition of the solution as shown by Abel (1), Skrabal (18), and Hahn and Clos (5). Atmospheric oxidation and the catalytic effect of light are also recognized as factors.

The stability of the solution prepared by the procedure outlined below is probably due to the substantial exclusion of bacteria, carbon dioxide, and light as deterioration factors.

The approximately 0.1 *N* thiosulfate stock solution is prepared as follows:

The distilled water for the solution is placed in a Florence flask, or some other glass container that will stand boiling over a flame. A rubber stopper, with suitable connection for a buret and with soda-lime tube attached, is inserted loosely in the mouth of the flask. The flask is then placed over a gauze-covered flame and the water boiled for about 15 minutes. During this operation the soda lime should be protected from the steam. After boiling has stopped the thiosulfate crystals, 25 grams per liter of solution, are added and the stopper of the flask is pressed down firmly and secured. The connection for the buret should also be closed, so that any air drawn into the flask upon cooling will enter through the soda-lime tube, which should contain a cotton pad on either side of the soda lime. The thiosulfate crystals are dissolved by agitation and the solution is cooled. The buret, also fitted with a soda-lime tube, is attached and the solution is protected from light.

The thiosulfate solution is standardized essentially as described by Bray and Miller (3). The procedure is as follows:

A 0.1 *N* solution of potassium dichromate is prepared by dissolving 4.9035 grams of potassium dichromate, which has been recrystallized 2 or 3 times from water and dried for 48 hours at 110° C., in distilled water and diluting to 1 liter. Twenty-five milliliters of the dichromate solution are transferred to a 1-liter flask containing 2 grams of potassium iodide dissolved in 70 ml. of water, with 3.4 ml. of 6 *N* hydrochloric acid added for acidification. After standing in the dark for about 10 minutes, the solution is diluted to 500 to 600 ml. and titrated with the thiosulfate solution, with about 3 ml. of starch solution added as the indicator very near the end of the titration. The solution turns from blue to green in color at the end point. The normality of thiosulfate solution is calculated on the basis of the dichromate solution as exactly 0.1 *N*.

Other reliable methods of standardizing the thiosulfate solution are available. Before adopting a method at least two of the recognized methods should be employed in parallel. This comparison will enable the operator to prove the accuracy of the method preferred for continued use.

The thiosulfate solution is diluted to 0.01 *N* strength, preferably with freshly boiled and cooled water, for use in standardizing the iodine solution and in the ascorbic acid titration procedure. The 0.01 *N* solution deteriorates relatively fast and hence should be prepared fresh each day. The stock solution maintains its strength for several months.

## Discussion

The iodine titration procedure outlined above differs from the ordinary iodine technic in two essential respects—namely, the high acidity under which the titration is carried out and the double back-titration.

Sufficient sulfuric acid must be added to lower the pH to about 0.02 to 0.08 to obtain a sharp end point. Lack of acid causes a sluggish titration and an indefinite end point. Fur-

thermore, in the presence of the high acidity, iodine is more nearly specific for vitamin C. The amount of acid recommended is near the upper limit for obtaining a satisfactory titration.

The work of Fujita and Iwatake (4), Musulin and King (15), Mack and Tressler (11), Lorenz (10), and others on the use of metaphosphoric acid in the chemical estimation of vitamin C indicates that the acid might be a satisfactory substitute for sulfuric acid in the iodine method.

Sulfuric acid in excessive concentrations may liberate free iodine from the potassium iodide present in the iodine solution but the quantity of acid recommended will not liberate sufficient iodine in 10 minutes to give a color with starch. The titration will, of course, be complete in considerably less time.

The procedure of adding an excess of iodine, then an excess of thiosulfate, followed by titration of the excess thiosulfate was adopted to improve the end point. If the titration is carried out directly with iodine, the reaction proceeds too slowly near the end, giving irreproducible results. By adding an excess of iodine all substances capable of being oxidized by the reagent under the existing conditions are oxidized quickly and completely. The added thiosulfate then reacts quickly and quantitatively with the excess iodine. Excess thiosulfate is used, then back-titrated with more iodine to the end point because in titrating solutions containing large amounts of colored substances, such as orange juice or tomato juice, the end point can be detected better by the appearance of the blue color than by its disappearance. The addition of a few extra drops of iodine solution after the reading has been taken shows definitely that the end point has been passed which is not possible when the end point is shown by the disappearance of color.

A large excess of iodine will result in a high titer, but this is not serious provided the excess does not exceed about 3 ml. The time the excess iodine is allowed to react is likewise not of particular importance if the reaction time does not exceed 3 minutes. The temperature of the solution is not important within the range of about 18° to 30° C.

The method must be used with caution in the estimation of ascorbic acid in canned juices. Higher than true values may be obtained, possibly because of the presence of ferrous iron and stannous tin. Misleading results may therefore be encountered in any canned juice when corrosion of the tin plate has occurred.

The essential oils of citrus fruits may interfere with the chemical estimation of vitamin C in juice products, causing slightly high results, but this source of error may usually be neglected.

The iodine method has the same limitation in the estimation of ascorbic acid in old oxidized products as the other chemical methods. Reversibly oxidized ascorbic acid, which is still biologically active, is not detected directly by the chemical methods. Various procedures have been offered for the application of chemical methods to the estimation of this form of the vitamin, but the methods are rather complicated for routine work and the uncertain evaluation of the result leaves much room for improvement in this direction.

The 2,6-dichlorophenolindophenol method and the improved iodine method give, on the average, nearly identical results with citrus juices. The iodine method is thus satisfactory for use in following the retention of vitamin C during the manufacture and storage of various citrus juice products. Its advantages are as follows: (1) It has a nonfading end point with a deep blue color that can be detected in the presence of any but the darkest colors. (2) Reproducibility of results is ensured by the definite nonfading end point. (3) Only common, inexpensive chemicals, available in almost any laboratory, are used. (4) The reagents employed can easily be standardized by well-known methods. (5) The reagent



employed are relatively stable and can hence be made up in large quantities, thus saving much time.

The 2,6-dichlorophenolindophenol method, with one of the standard procedures, should be employed for vitamin C exploratory work. For more or less routine control work, however, where it has been shown by trial that the modified iodine method gives substantially the same results as the 2,6-dichlorophenolindophenol method, the advantages of the iodine method commend its use.

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# Determination of Formic Acid

## A Simplified Procedure

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FORMIC acid is determined ordinarily, in the presence of other acids, by oxidizing with a mercuric salt and then determining the quantity of carbon dioxide evolved or the weight of mercurous compound produced. Recently Weihe and Jacobs (7) proposed mercuric acetate solution as an oxidizing agent because of its superiority over insoluble mercuric oxide. The use of an oxidizing agent in solution has a number of advantages: (1) It allows the oxidation to be carried on slowly and smoothly, thus preventing loss of carbon dioxide due to failure of the system to absorb a large amount of gas suddenly evolved; (2) it allows a close control of the amount of oxidant added; and (3) it prevents admission of carbon dioxide from the air during addition of the oxidant.

The behavior of a number of materials such as acetone, glycerol, ethanol, methanol, oxalic acid, lactic acid, furfural, ethaldehyde, etc., was studied by Weihe and Jacobs, who found that these substances did not interfere appreciably with the determination of formic acid. The error in the determination of pure formic acid was about 0.25 per cent. However, the apparatus was relatively complicated, requiring a mercury pump to recirculate the gases evolved through a lithium hydroxide solution in a closed system. Therefore it was felt that the usefulness of this method could be increased greatly by simplification of the apparatus.

Various methods of absorption have been used in determining the carbon dioxide evolved from formic acid (2, 4, 7). However, the fritted-glass absorber, used successfully for the absorption of carbon dioxide by Thomas (5), Wells, May, and Senseman (8), and Waugh (6), has not been used previously in the determination of formic acid. Since the use of an oxidizing solution such as mercuric acetate allows the oxidation to take place slowly, it was felt that the fritted-glass absorber would be ideal for absorbing the carbon dioxide produced. Furthermore, the use of strong solutions and a large excess of absorbents could be avoided, since Wells, May, and

Senseman have shown that under the conditions used less than a 10 per cent excess of 0.1 *N* sodium hydroxide solution was sufficient to absorb all the carbon dioxide evolved.

### Description of Apparatus

The glass absorber, *A* (Figure 1), consisted essentially of a glass tube 70 cm. long having an inside diameter of 1.8 cm. and provided with a fine fritted-glass disk, *B*, sealed into the bottom. A tube of this length permitted the use of as much as 75 cc. of solution without danger of loss by entrainment. Bruce and Bent (1) described a method of making such disks, which was modified by Wells, May, and Senseman (8). The manufacture of fritted-glass disks has been patented (3).

Absorber *A* was inserted through a No. 11 rubber stopper, *C*, with an outlet tube, *D*. The absorber fitted tightly but was lubricated with glycerol, allowing ready movement through the stopper. The absorption tube was connected to the vacuum, *L*, at the upper end by a stopper and tube, *M*. The stopper, *C*, fitted a soft-glass titrating bottle, *K*, of about 300-cc. capacity. A second stopper, *N*, provided with two openings, was used to close the flask during the titration and exclude atmospheric carbon dioxide (Figure 2).

A bent glass tube, *R*, approximately 2 mm. in internal diameter and long enough to reach nearly to the bottom of flask *K*, was used to introduce the titrating acid under the surface of the solution, thereby reducing the possibility of losing carbon dioxide during the titration. The tube was connected to the flask by a short piece of moderately heavy rubber tubing. The horizontal section was about 10 cm. in length to assure free movement of the flask. To reduce danger of diffusion, the tube was constricted to about 0.5 mm. at the tip. The oxidation flask was a 200-cc. three-necked, round-bottomed Pyrex flask, *E*, fitted with a Friederich condenser, *F*, a dropping funnel, *G*, and a tube, *H*. Tube *H* was slightly constricted at the lower end and connected at the upper end to a long soda-lime tube, *I*. The reaction flask and absorber were connected by a rubber tube, *J*. A screw clamp, *Q*, was used to regulate the vacuum. A spring clamp was used at *P* to prevent the liquid from backing up into *H*.

### Procedure

Introduce the sample, containing 50 to 100 mg. of formic acid, into flask *E*, dilute to 50 cc. with water, and add 5 cc. of *N* acetic



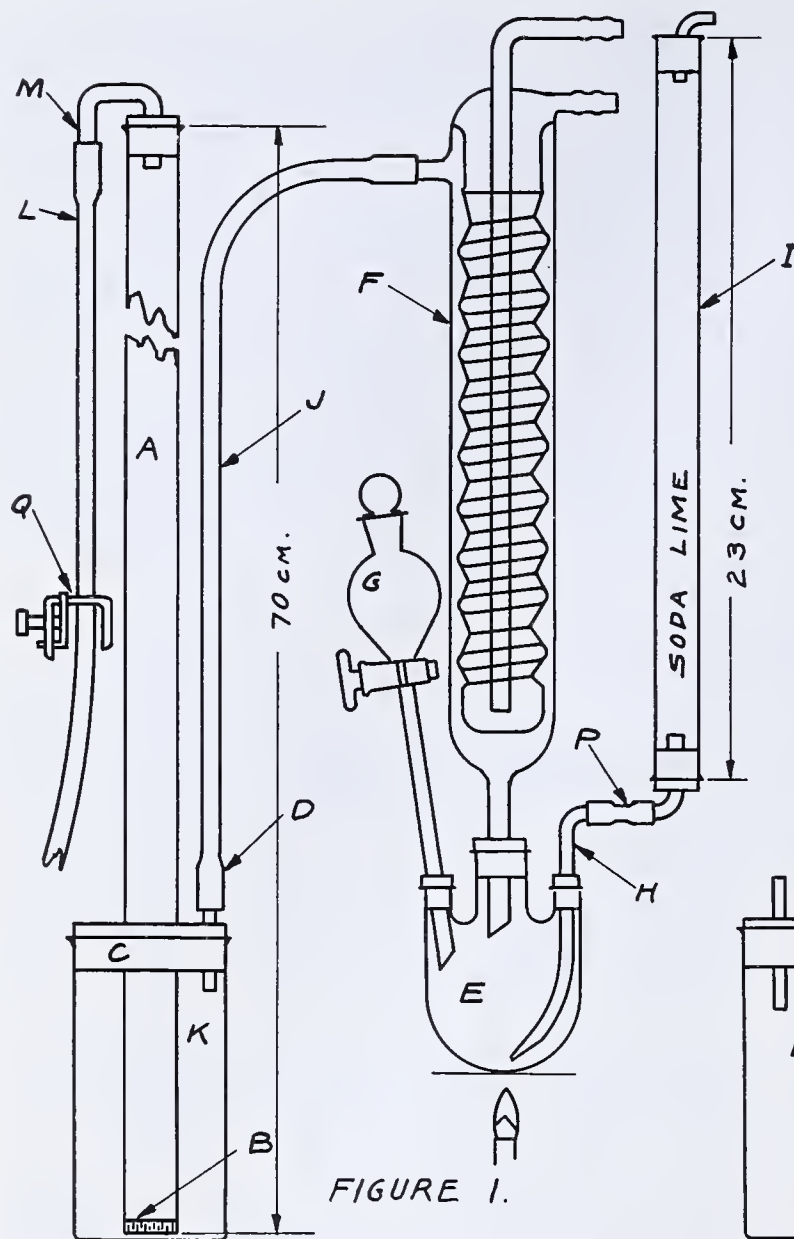


FIGURE 1.

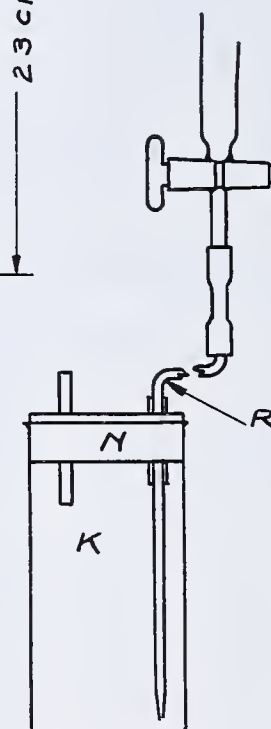


FIGURE 2.

acid. If necessary, a small particle of paraffin may be added to reduce foaming. Measure 20 cc. of mercuric acetate solution into the closed funnel, *G*. (The oxidizing solution, which was kept stoppered, was made by dissolving 100 grams of mercuric acetate in 1 liter of approximately 0.5 *N* acetic acid, and gently boiling for 1 hour to remove carbon dioxide.) With absorber *A* disconnected from the apparatus, connect the lower end of tube *J* directly to vacuum *L* and, by means of screw clamp *Q*, regulate the passage of air to about 200 to 250 cc. per minute.

Boil gently for 10 minutes to remove carbon dioxide, guarding against too vigorous boiling which may force the liquid back through tube *H* into the soda-lime tube, *I*. In the meantime place 4 drops of butyl alcohol in bottle *K* and follow by 50 cc. of approximately 0.1 *N* sodium hydroxide solution, which need not be previously standardized. Quickly connect bottle *K* to absorber *A* by means of stopper *C*. At the end of the 10-minute

boiling period remove the flame, attach a spring clamp at *P*, disconnect the lower end of tube *J* from the vacuum line, connect it to bottle *K* at tube *D*, and attach vacuum line *L* to tube *M*. Replace the flame and remove the spring clamp at *P*. When gentle boiling begins, allow the oxidizing solution in funnel *G* to drop slowly, over a 5- to 10-minute period, into the reaction mixture.

After 20 minutes remove the flame, attach the spring clamp at *P*, remove the stopper from the top of absorber *A* and tube *J* from *D*. Raise absorber *A* through the stopper sufficiently to clear the final volume of solution, but not far enough to prevent washing. Let the absorbing solution drain from *A*. (This may be hastened by gentle suction at *D* or better by a slight pressure applied through a soda-lime tube at the top of *A*.) Wash the tube with three 40-cc. portions of carbon dioxide-free hot water, draining each completely. Remove stopper *C* and quickly wash the bottom end of absorber *A*, allowing the washings to drain into bottle *K*. Close *K* immediately with stopper *N*. Add 10 cc. of 15 per cent barium chloride solution by pipetting it through one of the openings in *N*. Then add several drops of phenolphthalein. (This should not be added before precipitation, as it has a tendency to be occluded in the precipitate.) Before titration of the excess alkali, the tube (*R*, Figure 2) should be full of the acid solution and free from air which has a tendency to be trapped in the rubber connection. Titrate with 0.1 *N* hydrochloric acid solution, swirling the solution vigorously during the titration.

Correct for any carbon dioxide from the reagents used or introduced from the air by making a blank determination in exactly the same manner on 50 cc. of the alkali used. The difference in acid used is proportional to the formic acid content of the sample. (One cubic centimeter of 0.1 *N* hydrochloric acid is equivalent to 0.002 gram of formic acid.)

### Accuracy of Method

In Table I are recorded a number of results showing the efficiency of the absorption tube described using sodium carbonate solution and pure formic acid. In each case the end point was determined readily within 0.1 cc. and the error was found to be +0.33 per cent based on titration of the sodium carbonate solution. When pure formic acid was used an error of +0.40 per cent was found.

### Summary

A simplified and efficient procedure for the determination of formic acid is described, using a fritted-glass disk absorber to determine the carbon dioxide produced by the oxidation of the formic acid with mercuric acetate solution.

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TABLE I. DETERMINATION OF CARBON DIOXIDE FROM SODIUM CARBONATE AND FROM OXIDATION OF FORMIC ACID

Material Used	Carbon Dioxide in Sample		Difference Gram	Error %
	Calculated Gram	Found Gram		
Sodium carbonate	0.0905	0.0908	0.0003	+0.33
	0.0905	0.0908	0.0003	
	0.0905	0.0908	0.0003	
	0.0905	0.0908	0.0003	
	0.0905	0.0908	0.0003	
Formic acid	0.0994	0.0999	0.0005	+0.40 (av.)
	0.0994	0.0997	0.0003	
	0.0994	0.0999	0.0005	
	0.0994	0.0997	0.0003	



# Estimation of Boron by a Modified Flame Test

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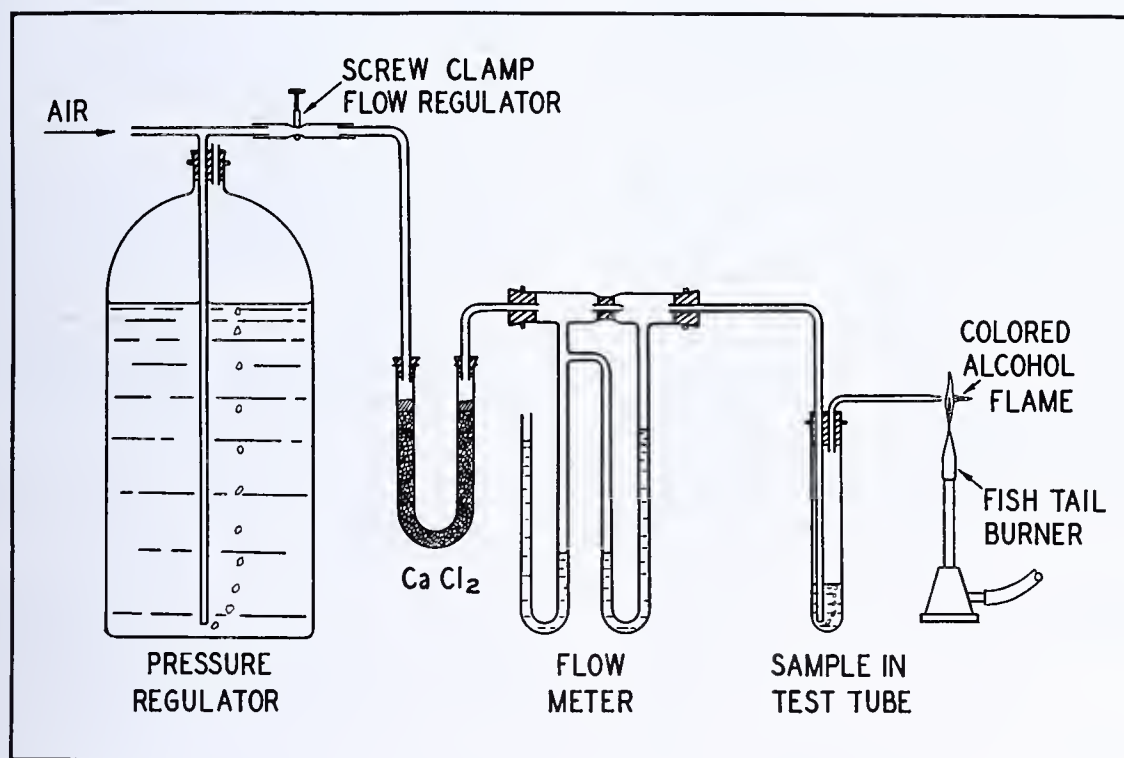
THE flame test, in which concentrated sulfuric acid and methyl alcohol produce a volatile boron compound, is commonly used for the detection of boron in some laboratories. The effects of the ratio of acid to alcohol, the temperature of the solution, and the amount of water present are presented by Stahl (1), who has devised a quantitative measurement of boron based on the intensity of the green coloring in the flame using a comparative standard. He claims an accuracy of 15 per cent.

Using the apparatus herein described, although the intensity of color in the flame diminishes at a marked rate when the amount of boron in the sample reaches 0.03 mg., the total time of duration of color is almost a straight-line function of the boron content up to about 0.1 mg. By successive dilution, a more concentrated sample of boron may be quickly analyzed, using this method.

equivalent of 0.02 to 0.10 mg. of boron in a test tube, evaporating almost to dryness, adding a mixture of 6 cc. of methyl alcohol and 1 cc. of sulfuric acid, and placing the test tube in the apparatus, a green color was imparted to the flame. The duration of the color was proportional to the amount of borate present. The results shown in Table I were obtained by these tests, the times to the end points being recorded on a stop watch, the dial of which had been covered.

TABLE I. ESTIMATION OF BORON

Boron Present Mg.	Observed Duration of Flame Sec.	Average Duration of Flame Sec.
0.02	80, 82, 80, 75	79
0.04	170, 140, 135	148
0.06	265, 255	260
0.08	355, 275, 310, 330	318
0.10	390, 315, 340, 365, 360, 370, 410, 420, 365, 355, 360, 350, 325, 375, 330	362



The figure shows the apparatus used. Air passes at a rate of 50 cc. per minute through a calcium chloride drying tube and flowmeter into the bottom of a test tube, where it bubbles through the 7 cc. of liquid containing the boron sample. A mixture of air, alcohol vapor, and methyl borate passes out the top of the test tube, through the nozzle, and through the thin part of a fan-shaped Bunsen flame, igniting and forming a small auxiliary flame at right angles to the other. It is this small flame that is colored distinctly green as long as an appreciable amount of methyl borate is present. The alcohol flame itself is blue-green, but the green imparted to the flame by the boron is quite different so that one has but little difficulty recognizing the end point. Observation of the flame at intervals of a few seconds is recommended rather than continuous observation. At that point when the constant blue-green of the alcohol flame is lost at two successive observations is taken as the end point. After a few trials this point is readily determined.

To check the accuracy of the method and its ease of application, an apparatus was assembled and operated by an experienced observer. Two standard solutions were made—one with 0.570 gram of boric acid, 2 grams of potassium hydroxide, and distilled water to make 1 liter, and the other by diluting 50 cc. of the first to 250 cc. One cubic centimeter of the first had an equivalent of 0.10 mg. of boron, and 1 cc. of the second, 0.02 mg. By placing a sample having the

The spread between the various tests is due in part to difficulty in holding the Bunsen flame in a single position. With a little practice an accuracy better than one significant figure may be obtained even for traces of boron, especially if the tests be carried out in a somewhat darkened room.

Difficultly soluble materials such as glasses are analyzed by fusing the sample in a nickel crucible with potassium carbonate, dissolving the fusion in distilled water, taking a suitable aliquot, and evaporating almost to dryness. The residue is acidified with sulfuric acid and then analyzed as outlined above. Even on glasses containing less than 1 per cent of boric oxide, checks of 10 per cent or better may be expected.

## Acknowledgment

The authors wish to thank W. T. Hall for his helpful suggestions.

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# A Simplified Quinhydrone Electrode

## Application in Determining the H-Ion Concentration of Liquids and Semiplastic Solids

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THE modifications in the design of the quinhydrone electrode and calomel half-cell described herein have been made to simplify the work of preparing electrodes and conducting pH determinations, to increase the accuracy of tests, and to increase the portability of the equipment.

### Apparatus and Procedure

**ELECTRODE.** The electrode consists of a platinum wire 10 cm. in length and approximately 0.6 to 0.65 mm. in diameter, or 22-gage (B and S), plated with gold.

**SAMPLE TUBE FOR LIQUIDS.** The sample vessel consists of a capillary Pyrex brand glass tube 7.5 cm. in length and 0.85 to 1.0 mm. in internal diameter, with a cup-shaped enlargement about 0.5 cm. in diameter at one end and with the other end flamed to about the same diameter as that of the electrode. A convenient method of selecting tubing is to use tubing into which a 20-gage (0.8-mm.) wire can be inserted but into which a 16-gage (1.3-mm.) or preferably an 18-gage (1.0-mm.) wire cannot be inserted.

**SAMPLE TUBE FOR SEMIPLASTIC SOLIDS.** The sample vessel for use with soft solids is that devised by Knudsen (3) and consists of a glass tube about 4 cm. in length and 3 to 4 mm. in internal diameter.

**PORTABLE CALOMEL HALF-CELL.** The essential parts of the cell are as follows:

A, an inner glass tube 6.5 cm. long and 3.5 mm. in diameter containing a copper lead-in wire welded to a short piece of 26-gage platinum wire, the latter being sealed through the lower end of the tube to conduct the current.

B, a glass tube 7 cm. in length and 9 mm. in diameter, sealed at the lower end to comprise the mercury-calomel chamber, and with a short piece of 26-gage platinum wire sealed through the wall at a point midway between the two ends. The sealed-in wire acts as a conductor and also prevents the escape of contents

from the mercury-calomel chamber; it is the essentially new feature in this cell and makes it possible to ship or transport the cell without damage.

C, an outer glass tube 7.5 cm. in length and 1.75 cm. in diameter, to the lower end of which is sealed a tube 4 cm. in length and 7 mm. in diameter with a 1-mm. capillary which is flamed to about 0.65 mm. at the tip end.

A lower glass cap 3 cm. in length and of the proper size to fit on a No. 0 rubber stopper.

To assemble the cell, 0.25 cc. of pure mercury and a small amount of calomel are placed in tube B. Tube A is inserted within B, and sufficient amounts of crystalline potassium chloride and saturated solution of potassium chloride are added to B nearly to fill it. A is then fastened within B by means of a rubber stopper. A thick layer of crystalline potassium chloride is placed in C and a sufficient amount of a saturated solution of potassium chloride is added nearly to fill the outer chamber. A small amount of ground glass, sifted to approximately 0.75-mm. mesh is added to the mixture of potassium chloride crystals and saturated solution of potassium chloride in the outer chamber, to prevent the escape of solid potassium chloride. Tube B is fastened within C by means of a rubber stopper. The two rubber stoppers at the top of the cell are so bored from one original stopper as to fit one within the other, and the top is finally sealed with wax. The lower cap, which should be nearly full of a solution of saturated potassium chloride, is kept in place on the cell when the cell is not in use, in order to exclude air from the capillary at the lower tip of the cell.

TABLE I. ELECTRODE READINGS OBTAINED

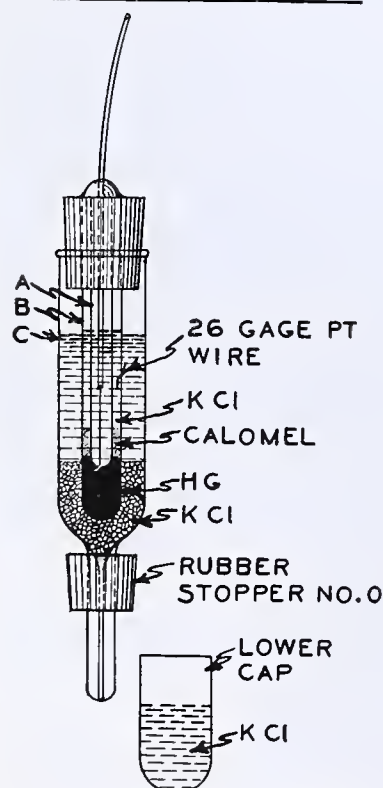
(With new type electrodes and with glass-sleeve electrodes in standard acetate buffer, pH 4.618)

New Type Electrode No.	Electrode pH reading	Glass-Sleeve Electrode No.	Electrode pH reading
1	4.61	6	4.61
2	4.62	7	4.61
3	4.62	8	4.63
4	4.61	9	4.63
5	4.60	10	4.61

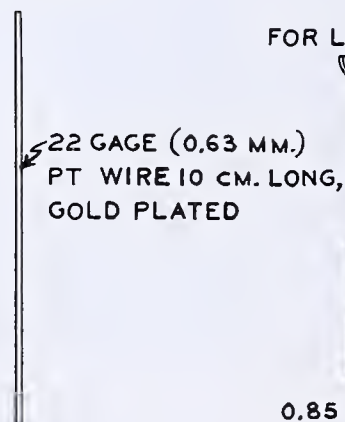
A diagram of the equipment described above is shown in Figure 1. The calomel half-cell differs from other calomel half-cells in that it is small and compact and can be transported without damage, and also in that the electrical current is conducted from the mercury-calomel chamber to the solution of potassium chloride in the outer chamber by means of a platinum wire sealed in the wall of tube B as shown in Figure 1. This sealed-in wire serves not only as a conductor, but also to retain the contents within tube B, a function which has been accomplished in other cells by the use of a stopcock or plug of cotton, asbestos fiber or agar.

**DETERMINATION OF pH IN LIQUIDS.** The capillary sample tube described above is rinsed with the test liquid by immersing the tip of the tube in the liquid and moving the tube upward and downward, the tube being held in a nearly horizontal position.

### PORTABLE CALOMEL HALF-CELL



### ELECTRODE



### SAMPLE HOLDERS

#### FOR LIQUIDS



0.85 MM. I. D.  
7.5 CM. LONG

#### FOR SEMI-PLASTIC SOLIDS



4 MM. I. D.  
4 CM. LONG

FIGURE 1. DIAGRAM OF ELECTRODE EQUIPMENT  
Calomel cell, electrode, and sample vessels for pH determinations



position. Quinhydrone is applied to the electrode by any one of the three following methods: (1) A small amount of quinhydrone is mixed with the test liquid. (2) The electrode is wetted in the test liquid and dipped into quinhydrone crystals. (3) The electrode is wetted and dried alternately by dipping it into a saturated solution of quinhydrone in acetone, a layer of quinhydrone crystals thus being deposited on the surface.

The electrode, which is bent slightly so that it retains its final position within the tube, is inserted into the tube and the tip of the tube is immersed in the test liquid. The electrode is now moved upward and downward within the tube and capillary force causes the liquid to rise nearly to the top of the tube. The tip of the tube, with the lower end of the electrode at a point about 5 mm. above the lower end of the tube, is then immersed slightly below the surface of a solution of saturated potassium chloride which is contained in a small beaker, the lower tip of the calomel cell being also immersed in the same solution. With the lead-in wire of the calomel half-cell connected to the proper wire leading to the potentiometer, the other potentiometer wire is now connected to the top of the electrode and the voltage is read. The connections are made in the manner described by Watson (8). The complete circuit is as follows: potentiometer, wire to calomel cell, calomel cell, saturated solution of potassium chloride contained in a small beaker, capillary sample tube containing sample and electrode, and wire to potentiometer. The solution of potassium chloride in the beaker, in which both the tip of the calomel cell and the tip of the sample tube are immersed for making readings, must be removed and the beaker must be cleaned frequently.

After being used, the sample tubes are cleaned in soap solution and rinsed in distilled water. A 26-gage copper wire is used in cleaning the tubes and excess moisture is finally removed from the tubes by suction.

DETERMINATION OF pH IN SEMIPLASTIC SOLIDS. Two or 3 grams of test material are ground in a mortar with about 0.05 gram of quinhydrone. The sample tube is filled by tapping one end into the mixture in the mortar. The electrode is inserted into the sample in the tube to a depth of about 5 mm. above the lower end of the tube and the reading is made as described above.

Accuracy

A large number of comparative determinations has been made in the same solutions and test materials, over a period of several years, to test the accuracy of the new electrode as compared with that of the conventional glass-sleeve type designed by Cullen and Biilmann (1,2). Electrodes of the latter type were made by welding 22-gage platinum wires to copper wires and sealing the former into tubes of special glass known as No. 881 Corning Normal Tubing, then filling the glass sleeves with paraffin. Representative data from a series of tests with gold-plated electrodes are shown in Table I. The results have shown that the accuracy of the new type electrode is equal to that of the conventional type. In tests in various dairy food products, principally milk, whey, and cheese, duplicate readings correspond within 0.01 to 0.02 pH unit.

Long-continued use of the electrodes in testing milk and cheese samples has shown that cracks in the glass seals of

glass-sleeve electrodes and failure to plate platinum electrodes with gold are frequently sources of error. This observation is in corroboration of results reported by Morgan and associates (4) and by Watson (8); the results indicate that while these factors may be negligible as sources of error in testing pure solutions, they become very important when organic materials of a complex nature are being tested. Watson (8) has previously shown that gold plating is essential in preventing and correcting poisoning of electrodes when samples of cheese are being tested. The data in Table II indicate the extent of the errors caused by cracks in the glass seals and by failure to plate platinum electrodes with gold.

Discussion

The accuracy of the new electrode has been found to be within 0.01 to 0.02 pH unit. The percentage of defective electrodes, which is high among those of the conventional type, has been greatly reduced in the new type; such inaccuracies as result from cracks in the glass seal and the development of other defects incident to the use of the glass sleeve have been eliminated. The electrodes rarely become defective during use and when one is found to yield inaccurate values it is only necessary to replate it. The work of preparing electrodes is greatly reduced and breakage is entirely eliminated. Tests may be made in as little as 2 drops of liquid. The small size of the capillary has the further advantages that temperature equilibrium is attained almost instantly, a minimum amount of surface area of the sample is exposed to the air, and a large proportion of the surface of the electrode is in contact with the test material.

The modifications presented have resulted from work previously described in abstract form (7) in which the pH of cheese and other materials was obtained by inserting the quinhydrone-coated electrode into the test material and making the reading directly. Since no method has been found for removing the trace of quinhydrone which is deposited in the test material, the direct measurement by means other than with a glass electrode is considered inapplicable to food materials and has been abandoned.

There has recently been described a quinhydrone electrode and auxiliary equipment (5, 6) for use in piercing tissues to the source of the fluid to be tested and for determining the pH of physiological fluid thus extracted. The equipment resembles that described herein in that a plain wire (36-gage) electrode is used; it differs in that its special application is in the withdrawal and testing of physiological fluids, while the equipment described above has general application in the testing of liquids and semiplastic materials.

Summary

Modifications of the quinhydrone electrode, sample vessel, and calomel half-cell are described, in which a plain gold-plated platinum wire is substituted for the conventional glass-sleeve electrode and in which a sealed-in platinum wire is substituted for a stopcock in the calomel half-cell. The application of the new electrode and portable half-cell in determining pH values of liquids and semiplastic materials is described.

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TABLE II. ELECTRODE READINGS OBTAINED

With new type electrodes and with glass-sleeve electrodes in daily use in testing samples of milk, whey, and cheese—test solution, standard acetate buffer, pH 4.618)

Type of Electrode	Unplated Platinum			Gold-Plated Platinum		
	No.	When pre- pared	After one month's use	No.	When pre- pared	After one month's use
New	1	4.61	4.60	9	4.61	4.61
	2	4.62	4.65	10	4.61	4.60
	3	4.63	4.64	11	4.62	4.63
	4	4.61	4.59	12	4.61	4.63
Glass-sleeve	5	4.58 <sup>a</sup>	..	13	4.62	4.63
	6	4.61 <sup>a</sup>	4.66	14	4.61	4.62
	7	4.62	4.59	15	4.63	4.61
	8	4.61	4.59	16	4.63	4.63

<sup>a</sup> Cracks developed in the glass seals in two of eight electrodes.



# Determination of Carbon and Hydrogen

## A Compact, Movable, and Easily Built Combustion Train

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**D**URING their research the authors needed a fairly rapid and reliable method for the analysis of compounds containing carbon and hydrogen, which would give consistent results with a moderate amount of training on the part of the operator and which did not have to be in constant use and adjustment.

The micromethod could be used successfully only if proper space and conditions were permanently available for the rather expensive microbalance and unwieldy combustion train (6). Moreover, unless a well-trained analyst is constantly engaged in microanalysis of carbon and hydrogen consistent results cannot be expected.

The macromethods which use samples of about 200 mg. are too slow, no more than one or two analyses being carried out in one day. Although good results can be obtained more consistently than by the micromethod by a less trained operator, error is introduced because of the large amounts of oxygen or air used to burn so large a sample. An error in one analysis means that a whole day's work has been wasted.

Therefore a study was undertaken in order to develop an apparatus for the analysis of samples large enough to be conveniently weighed by the macrobalance but small enough to ensure rapid combustion. As 50 mg. can be weighed with an accuracy of 2 parts per thousand on a macroanalytical

balance, this sample was chosen as the lower limit in size. After a careful study the upper limit of about 125 mg. was taken, as the largest sample which can be burned completely in a combustion train within 2 hours, and about 70 mg. was decided upon as a convenient sample.

Systems for the combustion of samples of such magnitude have been reported (1-5), but all have some disadvantage which renders them of little value for the authors' purpose. (1) It is assumed that a permanent place, usually a long desk, in the laboratory can be devoted exclusively to the analysis, whereas in view of limited space the authors needed a compact train which could be lifted and placed under the table without dismantling the apparatus. (2) These methods have the common error of neglecting to measure the volume of the gas used. The importance of this factor has been fully appreciated in microanalysis but not in macroanalysis. The authors found that when the time and bubble rate were controlled, they could not attain the reproducibility that could be realized by actually using a measured quantity of oxygen.

### Requirements of Apparatus

In order to overcome these difficulties an apparatus was built which had the following specifications.

**COMPACTNESS.** Figures 1 and 2 indicate how a compact and movable apparatus was secured. A single straight tube replaces the usual series of absorption tubes as scrubber for the elimination of water and carbon dioxide after the oxygen has passed through the preheater. By leading the train back and forth, the apparatus is made to occupy a space equal to the length of the combustion tube. When the tubes for absorption of carbon dioxide and water have been removed and stored in a desiccator, the whole apparatus can be lifted with one hand and conveniently stored without disturbing any of the setup, other than to disconnect it from the oxygen tank.

**REPRODUCIBILITY OF RESULTS.** On careful study, it was found that, if a slight modification of the Pregl "universal filling" (6) were used, practically any substance usually encoun-

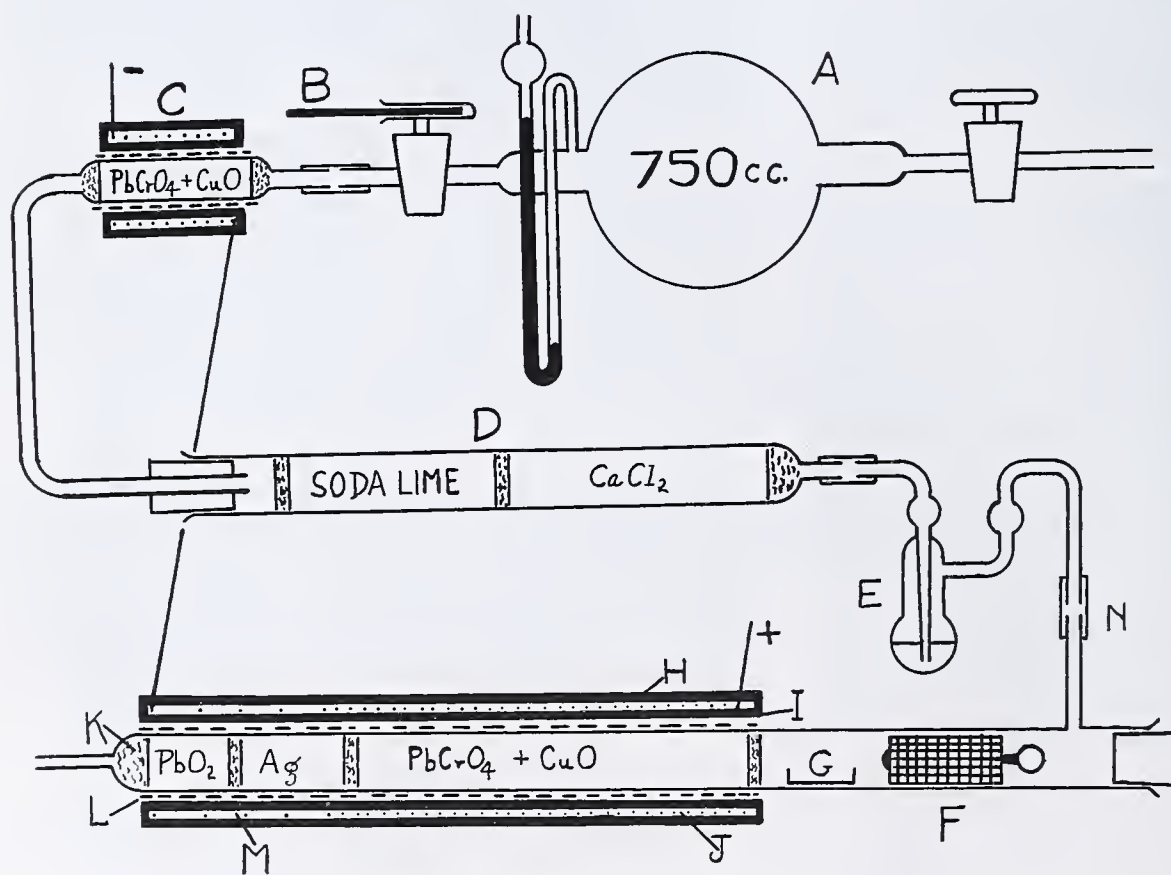


FIGURE 1. DIAGRAM OF APPARATUS

- A. Gasometer
- B. Stopcock lever
- C. Preheater
- D. Scrubber
- E. Bubble counter
- F. Copper oxide spiral
- G. Platinum boat

- H. Aluminum-painted asbestos
- I. Inner asbestos insulation
- J. Heating coil
- K. Asbestos plug
- L. Iron or Nichrome gauze
- M. Heating coil widely spaced
- N. Connection (at right angle to page)



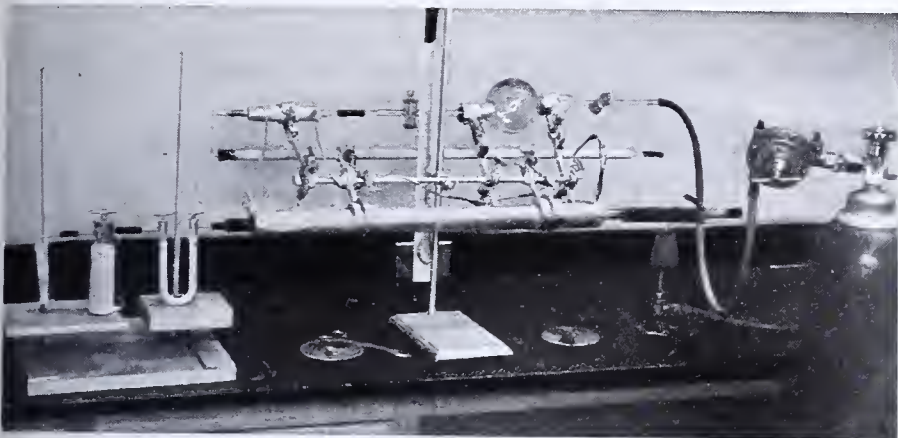


FIGURE 2. PHOTOGRAPH OF APPARATUS

tered could be completely burned. It was then observed that, on regulating the bubble counter and controlling the time, there could be as much as 100 per cent difference in the volume of oxygen used in two successive combustions, results were not consistent, and only an individual who had worked for some time with the apparatus could obtain reproducible results. It was decided, therefore, to include a gas-measuring device in the outfit. The Mariotte flask (6) was discarded because it is unwieldy, has no place in a movable apparatus, and reduces the pressure in the train so that it has a tendency, unless carefully controlled, to drag over incompletely burned vapors. These disadvantages were overcome by using a light gasometer, as shown in Figure 1, which may be placed behind the combustion train to drive the gas through under slight pressure. This same gasometer may be used in the Dumas nitrogen determination to measure the amount of carbon dioxide used.

**Low Cost.** The entire apparatus can be built from material usually found in the laboratory. Pyrex tubing may be used throughout. Earlier experimenters avoided Pyrex tubing as having too low a softening point, probably because of the tendency of an inexperienced operator to overheat the tube with gas flames. The authors have seen numerous cases where even the hardest glass has been badly distorted because of superheating, and if the Pyrex tube is heated directly by a roaring flame during the combustion the glass will easily distort under the internal pressure. If, however, the tube is encased in a short length of iron gauze and a moderate blue flame is used, the tube will last indefinitely. A temperature of  $550^{\circ}\text{C}$ . is adequate to burn most organic substances in a stream of oxygen and in the presence of lead chromate and copper oxide. When the apparatus is to be used by students, harder glass should be used or the flame replaced by a small independent heating unit, 8 cm. in length, set at  $50^{\circ}\text{C}$ ., which may be slid back and forth. This unit is easily built as described below.

More expensive combustion tubes of silica, Bohemian glass, hard Corning glass, and Supremax glass have been used, and have an advantage in their resistance to superheating and in that the combustion may be carried out more rapidly at a higher temperature ( $650^{\circ}\text{C}$ .).

The authors are still using a Pyrex tube which has been in continuous service for several months. This tube, at  $50^{\circ}\text{C}$ ., has expanded under the internal pressure to fit the surrounding wire gauze snugly, without impairing its efficiency.

This combustion train is recommended especially for the organic chemist, who can usually obtain more than 50 mg. of material for analysis and who wishes a method which will give consistent results without special effort. It is also recommended for students or as a teaching device for organic analysis where space is limited, only macrobalances

are available, and consistent results are sought by the less skilled analyst. The apparatus does not lose its accuracy if not in continuous use. It can be built, when materials are available, in 1 or 2 days.

The authors attempted to analyze samples as small as 2 to 3 mg. with this apparatus, using a microbalance and microabsorption tubes. Although preliminary results were encouraging, it was decided, in order to cut down on the amount of oxygen used and make the apparatus even more compact, to use the usual sized combustion tube and build the coils to its size. This tube and coils could then be used interchangeably with the semimacro-combustion tube and its coils. (Since the preparation of the original manuscript, the authors have received the cooperation of the Empire Laboratory Supplies Company, New York, N. Y., in the preparation of a compact and efficient instrument for the determination of carbon and hydrogen on both micro- and macrosamples. The details and results of this investigation will be reported later.)

### Building the Combustion Train

**HEATING COILS.** The electric heater for the combustion tube is prepared as follows: A strip of iron or Nichrome gauze,  $65 \times 8$  cm., is cut from a roll of ordinary laboratory gauze, and is bent around a long cylindrical piece of wood or glass tube, by gently tapping with a mallet, to form a cylinder 65 cm. long and of such diameter (approximately 2 cm.) that a tube of 16-mm. internal bore can be easily slipped in or out. The cylinder is made firm by binding at several places with soft iron wire. A strip of asbestos, slightly larger than the wire gauze and 0.6 cm. thick is soaked in water to make it soft and workable, and is pressed around the iron gauze cylinder to cover it completely. Smaller strips may be used, but all the gauze must be covered.

The asbestos is kept in place by the heating coil which is wound in the following manner: A single turn of soft iron wire is fastened around one end of the asbestos-covered cylinder, and to it is attached one end of a 6.5-meter (20-foot) Nichrome wire (B. and S. gage No. 22). A small piece of Nichrome wire is allowed to extend for purposes of electrical contact. The wire is then wound tightly around the cylinder with about 1 cm. between successive turns, until all but the last 12.5 cm. (5 inches) has been covered. The last turn is anchored with a turn of iron wire. Electric current is now sent through the whole length of the wire to dry and fix the asbestos in place. A thick paste is made of powdered asbestos (sells as asbestos cement for 5 cents per pound) and water. The cylinder is suspended by a tube going through the center and, except for the 12.5 cm. (5 inches) not covered with Nichrome wire, is evenly covered with asbestos paste to a thickness of about 2 cm. The current is sent through the whole length at short intervals, until the asbestos has dried to a semihard mass.

When dry, the asbestos covering is coated with several layers of aluminum paint (the kind used to silver radiators), which are dried by passing the electric current through the Nichrome coil. Some of the paint is absorbed in the asbestos and acts as a binder, making a hard surface. If a harder coating is desired, a small amount of any standard furnace cement may be added to the mixture of powdered asbestos and water. This gives a remarkably tough and light-weight coat. The aluminum paint prevents radiation from the coil, increasing the efficiency of the outfit and making it more comfortable for the operator.

In order to adjust the temperature in the cylinder, one contact is passed back and forth along the unused Nichrome wire. A temperature of approximately  $550^{\circ}\text{C}$ . is desirable with Pyrex glass and  $650^{\circ}\text{C}$ . with harder glass. Higher temperatures tend to fuse the lead chromate into the glass and considerably lower temperatures make for incomplete combustion. If a suitable pyrometer is not available, a sufficiently accurate adjustment may be made by sliding the contact along the wire until a red glow is seen along the center of the cylinder. Sufficient time (1 hour) must be allowed for the temperature to come to equilibrium. The contact is then moved so that the resistance is gradually increased until at about  $525^{\circ}\text{C}$ . the color definitely disappears. However, when a filled tube is inserted the temperature will rise markedly, for radiation is less than from the open tube. A Pyrex tube closed at one end by a rubber stopper may



be inserted and suction or pressure applied at the other end; if the Pyrex tube softens and distorts under pressure the temperature is too high. When the filled combustion tube is inserted and allowed to come to equilibrium, the temperature should be high enough so that when the tube is withdrawn the lead chromate has turned from yellow to deep orange.

When a suitable resistance has thus been decided upon, the Nichrome wire in excess of that needed for resistance is cut away and the remainder is used to make heating coils for the preheater and the lead peroxide. To keep the part of the cylinder not covered with Nichrome wire, at 200° C., so that the lead peroxide does not decompose because of too high a temperature or absorb moisture because of too low a temperature, the Nichrome wire is wound over it with turns about 3.75 cm. (1.5 inches) apart. The end is anchored with a turn of soft iron wire (these turns of iron wire need not be removed) after the coil is finished. This part of the cylinder is covered with powdered asbestos paste and dried and silvered as before. Its temperature is readily determined by means of an ordinary thermometer. A temperature variation of less than 5° (195° to 200° C.) is easily obtained but, if unsatisfactory or not uniform, the powdered asbestos covering can easily be removed with a sharp instrument, and the turns rearranged and again covered with asbestos and aluminum paint to give the desired uniformity to the very end. The Nichrome wire, necessary as a resistance, is cut off, leaving a small length to act as contact. A preheating unit is made around a little cylinder of iron-wire gauze covered with asbestos, 16 cm. in length and 1.4 cm. in diameter, with turns of Nichrome wire spaced 1 cm. apart, coated with asbestos cement and aluminum paint as before. Any unused Nichrome wire may be used as a fixed resistance in series with the preheater and the main heating coil, thus maintaining the temperature all along the line as desired. A total of about 6 meters (18 feet) of Nichrome wire is necessary.

**COMBUSTION TUBE.** The combustion tube consists of ordinary Pyrex tubing 16 mm. in internal bore and 85 cm. long, sealed at one end to 3 cm. of tubing 3 mm. in internal bore and at the side, about 4 cm. from the other end, to a tube of similar bore. A tube of the same dimensions but of hard Corning glass is used for higher temperatures. This tube is filled, essentially in accordance with the Pregl universal filling. An asbestos plug is followed by 10 cm. of lead peroxide sealed in place by a second asbestos plug. The remainder of the tube is cleaned from any lead peroxide adhering to the side.

Silver foil is cleaned by immersing it in a solution of sodium bicarbonate in an aluminum container or in the presence of a piece of aluminum foil. The silver foil is washed with water, dried, cut up into narrow strips, and packed tightly into the tube for 10 cm., along the temperature gradient from the copper oxide-lead chromate mixture to the lead peroxide. It is secured with an asbestos plug, and the tube, for the length of the rest of the heating unit (36 cm.) is filled with the usual mixture of lead chromate and copper oxide. This is secured with an asbestos plug. One variation is to line the tube with 35 cm. of thin copper gauze, rolled to fit snugly inside the tube, before filling it with the mixture of lead chromate and copper oxide. On subsequently passing oxygen through the heated tube, the copper gauze is oxidized to copper oxide, leaving a thin film of copper oxide on the walls of the tube to protect it against the hot lead chromate.

**GASOMETER, PREHEATER, AND SCRUBBER.** A 750-cc. glass bulb is sealed at opposite ends to two stopcocks as in Figure 1. The pressure is read by a mercury manometer sealed to the apparatus. It is apparent that when the manometer reading,  $\Delta P$ , is 25 cm. in a container of volume  $V$  (750 cm.) the gasometer can deliver a volume,  $\Delta V$ , of 247 cc. at atmospheric pressure,  $P$ .

$$\Delta V = \frac{\Delta P}{P} \times V = \frac{25}{76} \times 750 = 247 \text{ cc.}$$

Each centimeter difference in the manometer reading is equivalent to approximately 10 cc. A 5-cm. margin of pressure is allowed to remain in order to keep the rate of flow constant in the bubble counter. In practice this gasometer will actually deliver 200 cc. of gas. To facilitate regulation of the rate of flow, the end of the hollow Pyrex stopcock handle is softened in a flame, drawn out with the aid of a pair of tweezers, and scraped down with a wire gauze to admit a long piece of wood or glass, to give leverage for delicate control. Once the rate of flow is set, the gasometer may be filled from the oxygen tank as often as necessary without changing the position of the regulating stopcock during delivery.

The gasometer is connected directly to the preheater, which acts to burn any organic particles in the gas. The gas is then freed of carbon dioxide and then water by passing it through a straight tube, of the same internal diameter as the combustion tube, filled half with soda lime and half with calcium chloride. Because of the relatively large amount of soda lime and calcium chloride used, this charge need not be renewed for long periods of time. The narrow end of this tube is attached by rubber tubing to a bubble counter whose inlet tube is at a 90° angle with the outlet tube. The outlet tube is then connected by a rubber tube directly to the side arm of the combustion tube. Wherever glass tubing is connected by means of rubber tubing, the glass ends must touch each other. The pressure-resistant rubber tubing is boiled in 10 per cent alkali, washed, and dried before use, but need not be impregnated with wax as for microanalysis.

The whole setup is mounted on one short ring stand by means of an iron rod, two rings, and several clamps (Figure 2).

**THE COMBUSTION.** A copper oxide spiral, 8 cm. long, made by winding copper gauze around a thick copper wire shaped at the end in the form of a handle, and heating in a stream of oxygen in the combustion train, is placed behind the boat containing the weighed sample. The tube to be heated by the flame must be encased in a short length of iron gauze and care must be taken, when the combustion tube is made of ordinary Pyrex, not to heat the glass tube directly or to use a roaring flame. The gauze should be heated to a dull red heat by a silent blue flame. A platinum boat may be conveniently made by folding about 1 to 2 grams of thin platinum sheeting or foil into the required shape and fusing the joints by heating the boat to redness and striking with the aid of screwdriver and hammer. Soda lime (2 per cent moisture) and calcium chloride (both 8-mesh) are used in the Nesbitt tube and the Schwartz tube, respectively (Figure 2).

One-half to one hour before the sample for analysis is to be introduced, the soda-lime and calcium chloride absorption tubes are attached and the coils are heated. At this time and all during the combustion, oxygen is sent through the apparatus at the rate of 3.5 cc. per minute. The bubble rate for the particular counter used is adjusted to deliver this volume. The absorption tubes are removed, allowed to remain in a desiccator for 15 minutes, and then weighed. Whenever the absorption tubes are not on the train, the outlet of the combustion tube is attached to a calcium chloride and soda-lime tube to keep moisture and carbon dioxide from the filling. The absorption tubes are returned to the train, the boat with about 70 mg. of sample is introduced, and the copper oxide spiral is put about 1 to 2 cm. behind the boat.

The Bunsen flame is brought slowly towards the boat, starting at the beginning of the copper oxide coil, the speed depending on the nature of the material. The material should be slowly distilled into the combustion chamber. After 15 minutes the flame should be under the boat, where it should be kept from 10 to 15 minutes or until the boat is clear of material, and then brought, gradually, up to the heating coil to clear the tube of material. This procedure is repeated twice. At the end of about 40 minutes, the flame is turned off and the washing is continued for an additional 45 minutes. The time of combustion varies with the

substance from about 1.5 to 2.25 hours. In all cases, exactly 500 cc. of oxygen are used for the combustion and the washing. If less time is used, the rate of flow is decreased. The absorption tubes are now removed, placed in a desiccator, and weighed at the end of 15 minutes. During this time a second weighed sample is introduced, after the original boat has been removed, and a second set of absorption tubes is attached, beginning a second combustion. In this manner, four combustions and sometimes five can be carried out in one day.

TABLE I

Substance	Formula	Sample Gram	CO <sub>2</sub> Found Gram	H <sub>2</sub> O Found Gram	C Found %	H Found %	C Calcd. %	H Calcd. %
Benzoic acid	C <sub>6</sub> H <sub>5</sub> ·COOH	0.0760	0.1915	0.0335	68.68	4.89	68.85	4.91
1-Cystine	[SCH <sub>2</sub> CH(NH <sub>2</sub> )-- COOH] <sub>2</sub>	0.0763	0.1930	0.0335	69.00	4.87	30.00	5.00
		0.0760	0.0835	0.0360	29.96	5.26		
		0.0715	0.0781	0.0315	29.81	4.89		
Nitrophthalic acid	NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (COOH) <sub>2</sub>	0.0710	0.1184	0.0175	45.47	2.62	45.49	2.37
		0.0757	0.1270	0.0183	45.75	2.68		
		0.0694	0.0887	0.0081 <sup>a</sup>	34.86	1.30		
2,6-Dichlorobenzoquinone-imido-chloride	O:C <sub>6</sub> H <sub>2</sub> (Cl) <sub>2</sub> :NCl	0.0716	0.0916	0.0076	34.88	1.18	80.35	5.35
o-Stilbene carbonic acid	C <sub>6</sub> H <sub>5</sub> :CH:CH-- C <sub>6</sub> H <sub>4</sub> ·COOH	0.0707	0.2075	0.0313	80.04	4.92		
		0.0707	0.2070	0.0310	79.88	4.88		

<sup>a</sup> Error in weighing so small an amount at least 2 per cent.



## Results

The results presented in Table I consist of consecutive runs on substances containing different groups with varying degrees of ease of combustibility and unusual properties, to illustrate the effectiveness of the filling. Benzoic acid sublimates readily and must be approached slowly. Nitrophthalic acid explodes and must be heated gradually. 2,6-Dichlorobenzoquinone-imido-chloride is slow in burning and the flame must be kept under the boat for from 20 to 30 minutes. The amino, nitro, mercapto, and halogeno groups are included as representative of compounds encountered.

## Summary

A compact, easily built combustion train for the determination of carbon and hydrogen in samples of organic compounds weighing from 50 to 125 mg. is described. The apparatus is mounted on one short ring stand, takes up little desk space, and can be easily moved to a convenient place without dismantling, when not in use.

The amount of gas used is measured by the introduction of a new type of gasometer. This makes results more consistent.

Heating is done electrically throughout (the boat may also be heated by a flame).

Pyrex glass may be used permanently for the combustion tube, when special care is taken and the temperature is kept at about 550° C. It is recommended that, when available, harder glass be substituted and a temperature of 650° C. be used for more rapid combustion.

Directions are given for constructing the heating coils from materials readily available. A single heating coil is used to heat the combustion tube at different temperatures, as needed at different parts of the tube.

An application of this setup, with some modification, to the analysis of microsamples will be reported later.

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RECEIVED December 9, 1937.

# An Improved Constant-Pressure Valve

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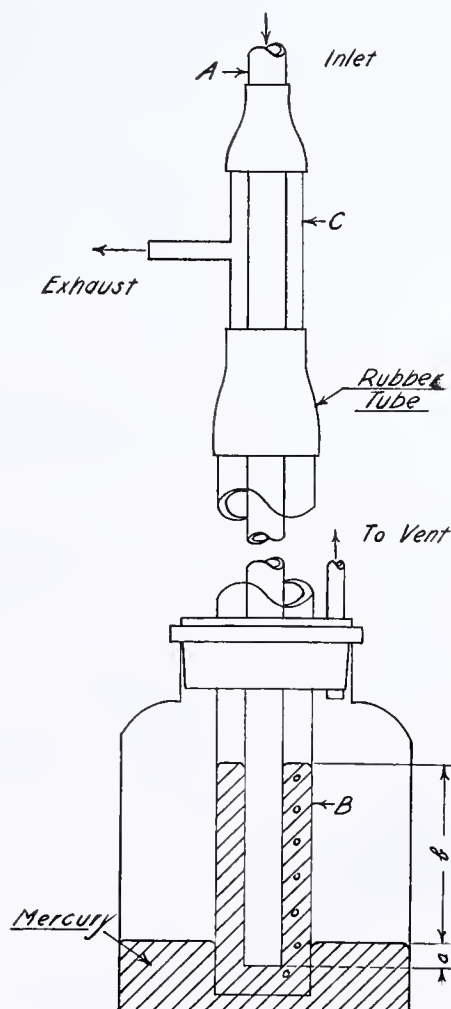
DURING the course of some recent experiments, it became necessary to remove a condensable gas, containing small amounts of noncondensables, from a generating system maintained at any desired constant pressure. It was necessary to liquefy as much of the condensable material as possible and remove the noncondensables while maintaining the generator in continuous operation. To permit the use of a vacuum pump for removing the noncondensables and yet maintain a constant pressure in the generator, a constant-pressure valve was needed and a mercury valve seemed to be a possible solution. However, no known form was found which would fill the above requirements.

The ordinary check valve (6) having a narrow inlet tube dipping below the surface of mercury in a larger tube, as well as the various U-shaped modifications of this type, was unsuitable because constant pressure on the fore part of the system can be maintained only if the back pressure is constant. Likewise, the Stock valve (7) using glass floats with ground ends to seal the tube even in its recent forms (1, 3, 5) suffers from the same defect. The recently developed check valve (2, 4, 8) using a thin layer of mercury on a porous plate has the same limitations. While a leveling bottle may be used to overcome these difficulties to some extent, such a device robs the valve of its simple automatic character.

A valve has been devised, however, which meets the above requirements of permitting gas removal at a constant pressure independent of the back pressure on the exhaust line. The valve permits gas take-off at pressures above or below atmospheric as desired, and serves also as a safety manometer to prevent excessive pressure in the system. Because of its applicability to various uses, particularly in vacuum distillations at constant pressure, a brief description of the valve appears desirable.

The construction and operation of the valve will be evident from the accompanying sketch. The gas enters through the inlet tube, A, whenever its pressure exceeds that represented by the height of mercury, a, and bubbles up through the mercury in the tube, B. The height of mercury, b, will depend on the

back pressure of the exhaust line. By raising or lowering the tip of tube A, the take-off pressure may be varied at will. In case of blocking of the exhaust, both mercury levels a and b will drop below the end of tube B and the gas will escape into the large container which is open to the air or to a vent. In order to





minimize the fluctuations in the take-off pressure, tube *B* should be as small as is possible without permitting entrainment of the mercury in the exhaust gas. (If desirable, a plug of cotton or glass wool may be inserted in tube *C* below the exhaust to prevent passage of entrained mercury.) The surface of the mercury in the outer container should be large, so that its level will not vary appreciably with changes in level *b*.

For a moderate gas stream, standard Pyrex glass tubing having the following outside diameters was used satisfactorily: *A*, 7 mm.; *B*, 15 mm.; *C*, 10 mm. A 500-cc. Erlenmeyer flask or ordinary bottle may serve as the container.

Obviously, the dimensions may be varied as necessary, glass inner seals may be used in place of the rubber connections, and liquids other than mercury may be used if desired. In some applications where permanent seals between the glass

tubes are necessary, a leveling bottle connected to the outer reservoir may prove advantageous in permitting operation under various pressure conditions.

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RECEIVED November 12, 1937.

## Preparing Fragile Paint and Varnish Films For Determination of Tensile Strength, Elongation, and Permanent Set

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SEVERAL physical properties of paint and varnish films, such as toughness and elasticity, have usually been determined only indirectly. Reduction with kauri, exposure and weathering tests, etc., are not always suitable for evaluating such properties. Preparation of the free film in a form which permits handling makes possible a direct examination of its properties. Two methods of preparing free films—stripping from the foundation (3) or dissolving the foundation with acid (1) yield films which may be tested in extensometers such as that of Gardner (2) or Tesson (4). For stress-strain measurements Nelson (3) prepared paint and varnish films by spraying or flowing on amalgamated tin plate (stating that brushing does not give satisfactory films unless the material has a sufficiently low yield value to permit brush marks to flow out). His films were 0.120 to 0.150 mm. thick for paints and 0.090 to 0.100 mm. thick for varnishes, about ten times the thickness usually found in practice. Furthermore, he had difficulty in obtaining films of uniform thickness. Most paint and varnish films are too thin, too soft, or too brittle to be handled by Nelson's method.

In the authors' method, the free film is prepared on a thin tin-foil foundation, enabling the operator to handle it easily until the test specimen is placed in the extensometer. There the test piece floats upon a bath of mercury which removes the tin-foil backing by amalgamation, leaving the free film in place for testing.

The film is made by pouring the material to be tested on a sheet of tin foil (0.001 cm. thick). To obtain a uniform film and to keep any material from reaching the back of the foil, which

would later prevent the amalgamation of the tin, the coated foil is hung from a 3.2-mm. (0.125-inch) horizontally fixed metal rod to which it is attached with paper clips. A similar rod is attached to the bottom of the foil and left free, thus keeping the panel vertical and smooth. After drying, the test piece is cut so that its long axis is at right angles to the direction of flow of the material. In any other direction there will usually be an appreciable variation in film thickness. A template in the form of the test piece is helpful in cutting the specimen and marking it for elongation measurements. Two holes, 40 mm. apart, are drilled in it and carbon black is rubbed gently over the holes to get the elongation marks on the film.

The apparatus for testing is a horizontal extensometer. The test piece floats upon mercury in a shallow dish (5 mm. deep, 40 mm. wide, 250 mm. long). The ends of the test piece are gripped by folded emery paper held in position with paper clips.

One grip is attached to a stationary support by a thin rubber band. The other is attached by a strong thread passing over a pulley to a light pan. The top of the pulley is on a level with the surface of the mercury. About half an hour is sufficient for amalgamation and then weights can be applied and measurements made. The progress of the amalgamation is usually visible.

Some determinations by this method are given in Table I.

### Discussion

Characteristics of paint and varnish films, the influence of age, humidity, and temperature, or the effect of new ingredients or a new procedure of production can be studied by this method. It offers a means for evaluating tough and elastic films, such as those called for by federal specification TT-P-51a and others.

This method can be used where the kauri reduction test is inapplicable because of incompatibility of the kauri solution and the vehicle of the material to be tested.

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RECEIVED January 19, 1938.

TABLE I. DETERMINATIONS

Material	Age of Film Days	Film Thick- ness Cm.	Total Break- ing Load Grams	Maxi- mum Elonga- tion %	Perma- nent Set %
Spar varnish, federal specification TT-V-121a	60	0.0020	35	17	..
Raw linseed oil, with 5% liquid driers	10	0.0015	6.5	20	19
Floor varnish, federal specification TT-V-71	68	0.0025	74+	0	0
Vehicle of flat ceiling paint <sup>a</sup>	68	0.0015	4.0	30	30

<sup>a</sup> Vehicle obtained by permitting pigment to settle.



# A Reciprocating Laboratory Shaker

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LABORATORY agitating devices may be divided into two main classifications: rotating devices and reciprocating devices.

In rotating devices, the container may be rotated about its own axis, about a line parallel to its axis, or about a line not parallel to the axis of the container—e. g., a line perpendicular to the axis of the container, giving an end-over-end motion. In all of these, as the container revolves about a horizontal axis, the liquid surface rises with the container and falls or slides back under the force of gravity, producing a tumbling motion. In rotating devices, the speed and radius of rotation are limited by the fact that when the centrifugal force on the liquid becomes equal to the force of gravity the liquid will remain at the wall of the container and rotate with it.

Reciprocating devices impart a much more violent agitation to the liquid in the container. The sudden reversals of momentum throw the liquid up the sides of the container, first one way, then the other. A type commonly encountered in chemical laboratories consists of a box with flasks held in place by spring steel strips. The box is driven by a crank and rocker arrangement.

## Construction of a Reciprocating-Type Agitator

During the course of investigations conducted at the M. I. T. Textile Laboratory on the electrical conductivity of cotton,

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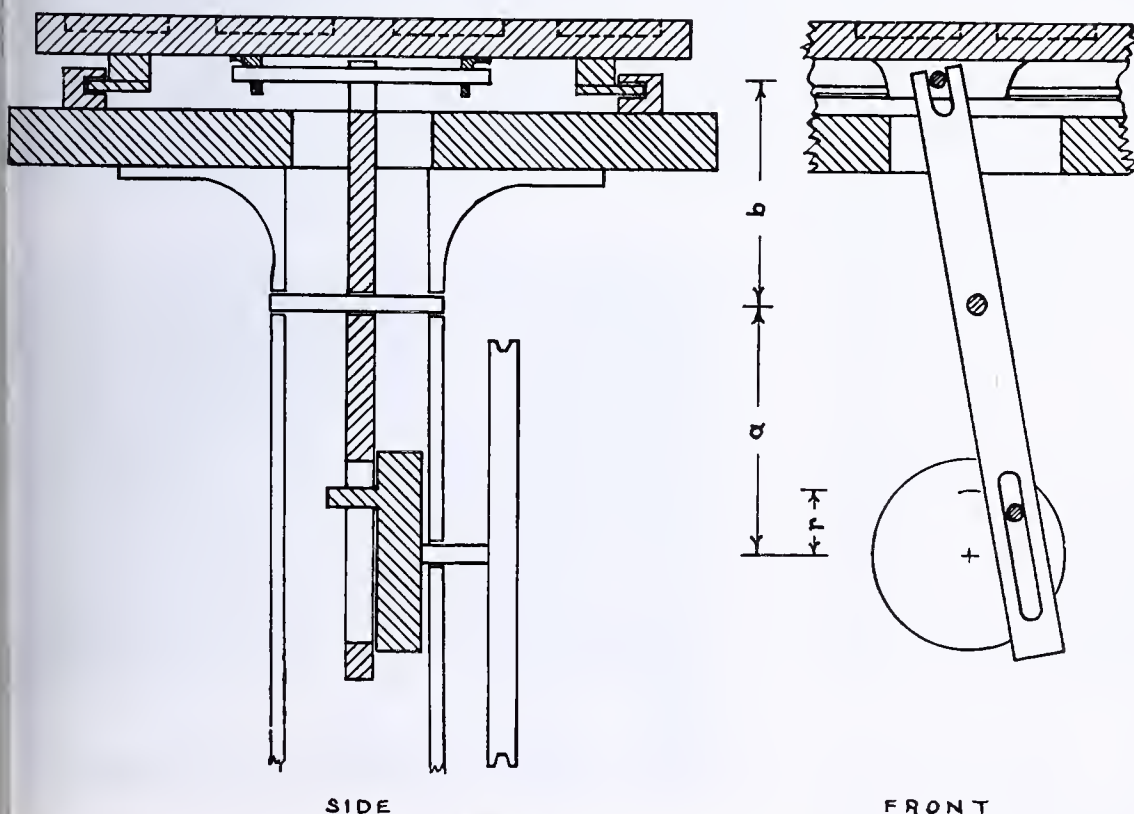


FIGURE 2. SECTIONAL VIEWS OF MECHANISM



FIGURE 1. AGITATING MACHINE

it was desired to wash samples of cotton in distilled water to remove electrolytic salts. Owing to the natural waxes present on untreated cotton fibers, it is exceedingly difficult to wet them out in pure water without the addition of surface-active ingredients. Since the addition of such materials might defeat the purpose of the research, it was found necessary to design an agitator which, by purely mechanical means, would displace the entrapped air in the cotton and permit wetting out.

The combined ideas of several members of the laboratory staff, together with the genius of a staff mechanic, finally resulted in the conversion of an abandoned cast-iron base and motor into a very serviceable agitating machine (Figure 1).

The machine carries sixteen 300-ml. Erlenmeyer flasks which are set into recesses in the carriage and then held firmly in place by a plywood board drilled to accommodate the necks of the flasks. The carriage is thrown rapidly back and forth by a crank-and-lever mechanism giving a quick-return motion.

Wetting-out of the cotton samples was complete in a few seconds, owing to the violence of the agitation, and the washing action was complete in less than 15 minutes. The agitator has also been used in special fabric-wash-



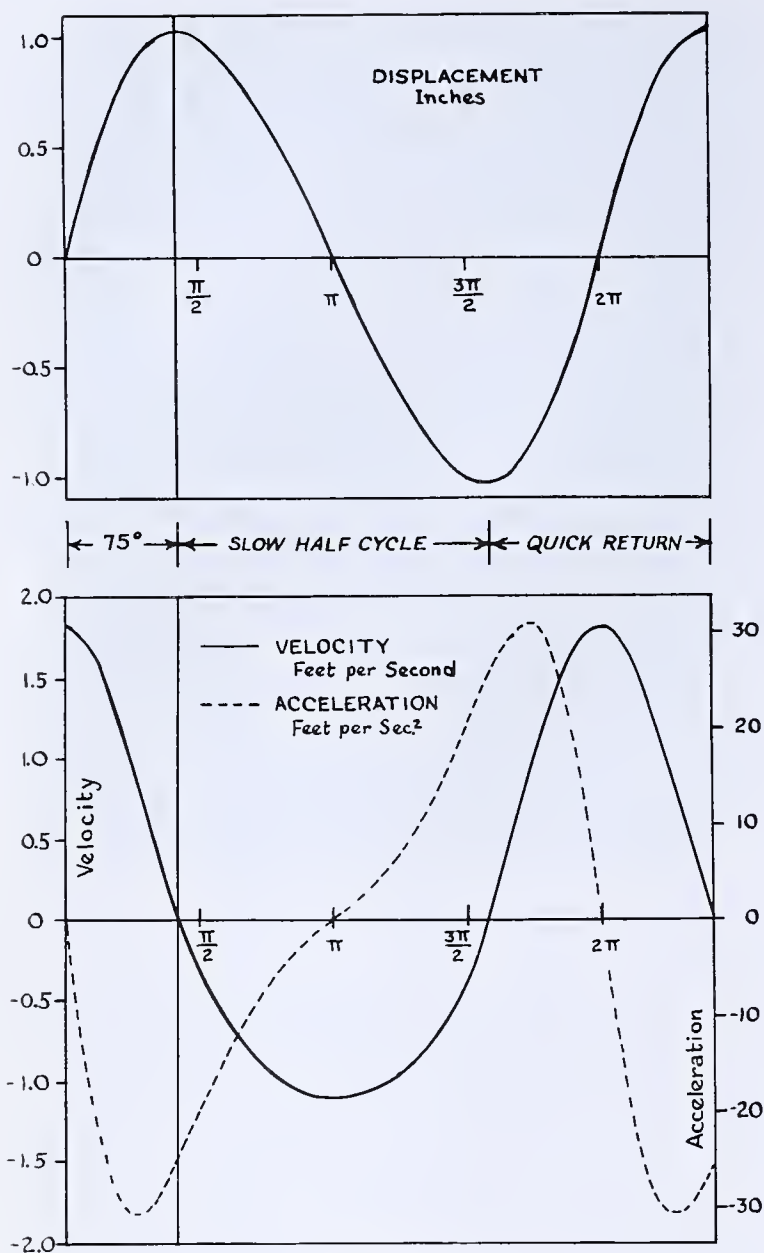


FIGURE 3

ing tests. Here, four 2-liter round-bottomed flasks were clamped into place, and the fabrics were placed in the flasks together with the desired amount of water and a number of rubber balls. The balls were thrown back and forth against the fabric, greatly augmenting the mechanical treatment of the goods.

Despite the violence of the agitation within the flasks, the machine, after having been bolted firmly to the floor to prevent "walking," ran with surprising ease and quietness. Upon occasions, it has been kept running for 10 hours at a time, and it has been in use for about 2 years without requiring mechanical attention.

**DETAILS OF MECHANISM.** The crank is driven from the motor through two pulleys giving a six-to-one speed reduction. (A 220-volt 0.1-horsepower motor was run at 110 volts to give an actual crank speed of 160 r. p. m.)

The lever is pivoted near its center and is slotted at both ends (Figure 2). One end accommodates the crank pin, while the other end engages a pin attached to the bottom of the sliding carriage.

The carriage rests on brass strips moving back and forth in slotted steel strips attached to the base. The arrangement is fairly evident from the sectional diagrams (Figure 2) and the photograph (Figure 1).

Three constants affect the motion of the carriage:  $r$  = radius of crank (to center of pin),  $a$  = distance from center of crank to pivot, and  $b$  = distance from pivot to line of motion of undercarriage pin. Assuming a constant angular

velocity in the crank, the displacement (from center position), velocity, and acceleration of the carriage have been computed for a complete cycle, using the values:  $a = 10$  cm. (4 inches),  $b = 10$  cm. (4 inches), and  $r = 2.5$  cm. (1 inch).

The maximum displacement occurs in this case when the crank has turned only  $75^\circ$  from the zero position (pin at top). The motion of the carriage to the right then takes  $210^\circ$ , while the return motion takes  $150^\circ$  (Figure 3). It is interesting to note that, while the slow half-cycle shows uniform acceleration changes, both the positive and negative peak accelerations are crowded into the quick-return half. These sharp acceleration peaks probably account for much of the efficiency of agitation of the mechanism.

The quick-return action could be augmented by decreasing the ratio of  $a$  to  $r$ . Thus, when  $a = 2r$ , the maximum displacement occurs at  $60^\circ$ . The two acceleration peaks are then greatly emphasized and occur in the short  $120^\circ$  portion of the cycle. The slow half-cycle takes exactly twice as long ( $240^\circ$  rotation).

The machine is oiled at several points to reduce friction losses: crank face and pin, pivot of lever, pin on undercarriage, and the slide supporting the carriage.

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## An Efficient Bottle-Shaking Apparatus

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THE apparatus described in this article was designed for use in an adsorption investigation in which a number of samples were to be shaken for a considerable length of time. The construction is simple and inexpensive, and the shaker has given excellent service in continuous use over long periods. Although designed originally for use with six 125-ml. Erlenmeyer flasks, it may easily be adapted to other types and numbers of containers.

The device consists essentially of a circular platform mounted at an angle of  $15^\circ$  upon a vertical motor-driven shaft to which it is joined through a ball-bearing joint. Three (or more, if desired) springs attached at the periphery of the platform and anchored to screw hooks in the base prevent the platform from

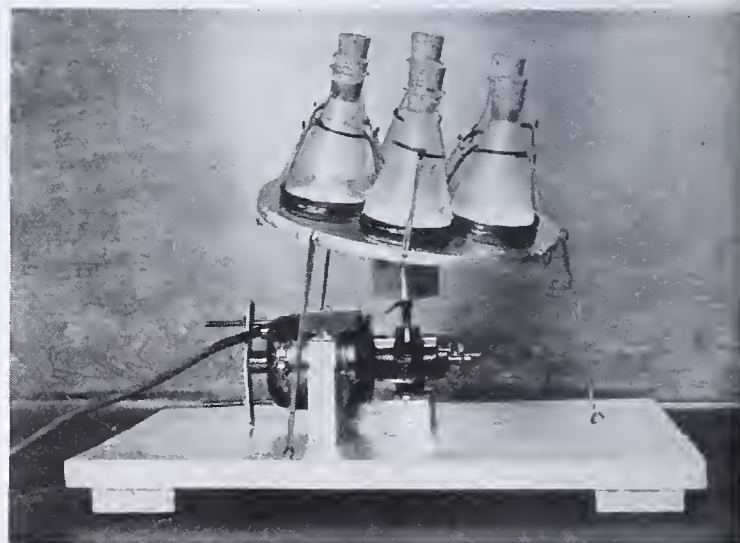


FIGURE 1. EFFICIENT BOTTLE-SHAKING APPARATUS



rotating, yet allow it to tip in every direction as the drive shaft rotates (Figures 1 and 2). The contents of containers or bottles mounted on the platform are shaken very effectively by this eccentric action.

Details of construction are shown in the illustrations. The motor used by the author is a Motorola phonograph attachment equipped with a built-in reducing gear and a vertical shaft. Other types of phonograph motors should be as satisfactory, and can generally be obtained on the second-hand market. The speed of the drive shaft should be about 100 to 200 r. p. m. for good results.

The ball bearing by which the platform is joined to the drive shaft is made from a steel chest caster with ball-bearing swivel joint. This type has a flat steel plate for fastening to furniture by wood screws. The wheel is removed and the frame cut down and drilled so that it can be bolted securely to a wooden block. The block is attached to the drive shaft as shown in Figure 2.

The flat plate of the caster is fastened to the platform with screws. The platform is 22.5 cm. (9 inches) in diameter and 1.25 cm. (0.5 inch) thick. A circular disk of wood, 7.5 cm. (3 inches) in diameter and 1.9 cm. (0.75 inch) thick, is mounted in the center of the platform. Six screw eyes in this block are used for fastening the flasks to the platform.

The metal cups in which the flasks are set are Kerr Mason jar rims. A ring made of No. 16 B. & S. wire, with two hooks soldered at diametrically opposite points, is slipped over the neck of a flask and anchored to screw hooks in the platform by means of several rubber bands.

The three springs which anchor the platform to the base may consist of several long rubber bands each, or of long coil springs. These springs must not be so powerful as to prevent motion of the shaker platform, and must be of equal strength.

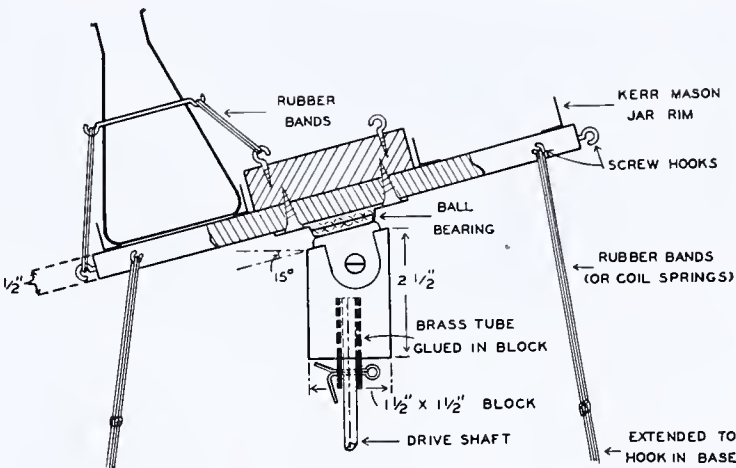


FIGURE 2. DETAILS OF SHAKING APPARATUS

The base on which the whole apparatus is mounted is of heavy lumber.

Careful selection of the motor is of vital importance to the success of this machine. A motor with good bearings, easily lubricated, and capable of running a long time without overheating is the ideal type. A rheostat may be used for a speed control.

RECEIVED March 7, 1938.

# An Improved Mercury U-Gage

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THE most widely used manometer for the measurement of moderately low pressures—for example, in vacuum distillations—is a U-shaped glass tube with one end sealed and filled with mercury. Its usefulness is based mainly on its simple direct indication of the absolute pressure which can easily be read at any moment.

It has, however, some objectionable features—for example, the necessity of boiling the mercury in the glass tube to remove the air from the closed reference limb when filling the gage and the ease with which air gets into the reference limb after short service, rendering it useless for accurate work.

The customary construction has the added drawback of inaccuracy due to capillary action on the meniscus of the mercury.

The modified gage described here has been designed to overcome these difficulties while preserving the desirable features of the U-gage, and is essentially a modification of the manometer recommended by von Rechenberg (4). Referring to Figure 1, A and B are the limbs of a U-tube, each having a diameter of 16 mm. Tube A, the indicating limb, is connected to the vacuum line in the customary manner. Tube B, the reference limb, however, instead of being sealed at the top, is connected to a capillary tube,

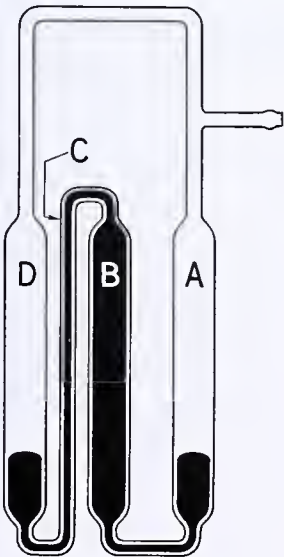


FIGURE 1

C, which in turn is joined to a wide tube, D, at the bottom. D is also connected to the vacuum line.

This connection of both the indicating and the reference limbs to the same vacuum line forms the fundamental difference from the ordinary U-tube manometer which has a closed reference limb. It greatly facilitates filling the gage and maintaining it in perfect working condition.

To get the gage ready for operation, mercury is poured through the side tube until A and B are about two-thirds full. It is then connected to a good vacuum pump and exhausted. By inclining it backward almost to a horizontal position and by tapping the glass sharply, the air adhering to the glass walls is brought to the surface of the reference as well as of the indicating column, and removed by the pump.

When no more air bubbles are visible under the reduced pressure at which the gage is to be used, it is tilted to the left until mercury flows over the top of B through C into D, thus removing the last traces of air from B and forming a seal which prevents air from getting into it again.

When the mercury level in A approaches the bottom, the gage is put back into its vertical position and the vacuum is released. The mercury will rise in C and B until the two columns flow together at the top of the bend, filling B and C completely. The levels in A and D should be about 20 mm. above the bottom, so as to form an effective seal.

The gage is now ready for use and may be connected to the apparatus in which the pressure is to be measured. As soon as the pressure is reduced to a value corresponding to the difference in heights of the mercury columns in A and B (or C and D), the mercury will separate at the top of the bend, between B and C, and as the pressure diminishes each part will recede in B and C until the levels become constant. The difference in height of the mercury levels in A and B indicates the absolute pressure.

For accurate and convenient reading of the pressure the gage may be provided with blackened metal sleeves which can be moved up and down over limbs A and B. When



viewed against diffused light the lower edges of the sleeves and the meniscus of the mercury show up against a white background as sharply defined straight and curved lines. When the sleeves are adjusted so that they seem to touch the tops of the mercury columns the absolute pressure is represented by the difference in height between the edges of the sleeves. (A gage with arrangements for reading to 0.1 mm. is manufactured by the Scientific Glass Apparatus Company, Bloomfield, N. J., U. S. Patent 2,075,326, March 30, 1937.)

The reasons for choosing a comparatively wide diameter for the limbs of the manometer are threefold:

1. The mercury meniscus is independent of forces of capillary attraction.
2. The visibility is greatly improved, even if the inside of the glass becomes dirty after long use. The production of a film on the glass can be minimized by avoiding contact of the mercury with rubber, by using clean mercury free from other metals (2), and by trapping dust and mist by an appropriate filter.
3. Air, which after long use or by too sudden release of vacuum may get into the reference limb, will collect at the top of the bend in *C*. If the air bubble has a diameter of 0.2 mm., a size clearly visible to the naked eye, its volume would be 0.42 cu. mm. at 7.6 mm. of mercury (0.01 atmosphere) and 4.2 cu. mm. at 0.76 mm. of mercury (0.001 atmosphere). As the cross section of *B*

is 200 sq. mm., the height of the air layer would be 0.0021 mm. at 7.6 mm. of mercury, and 0.0210 mm. at 0.76 mm.

The error caused in the reading would be 0.03 and 2.8 per cent, respectively. Even such small errors can be avoided by driving the air out of *C* in the following manner:

The gage is tilted to the right until the mercury level in *D* approaches the bottom, and is connected with the vacuum line while in this position. When the gage is evacuated, it is tilted to the left until the mercury flows over the top bend of *C*, pushing the air out into *D*. When the level in *A* approaches the bottom, the gage is put back in its vertical position.

For correct reading it is necessary to have the gage in a perfectly vertical position. Other precautions to be observed, especially for pressures of 2 mm. and less, have been discussed repeatedly in the literature (1, 3).

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RECEIVED February 12, 1938. Journal Series paper of the New Jersey Agricultural Experiment Station, Department of Agricultural Biochemistry.

## High-Vacuum Fractional Distillation without Gravitational Reflux

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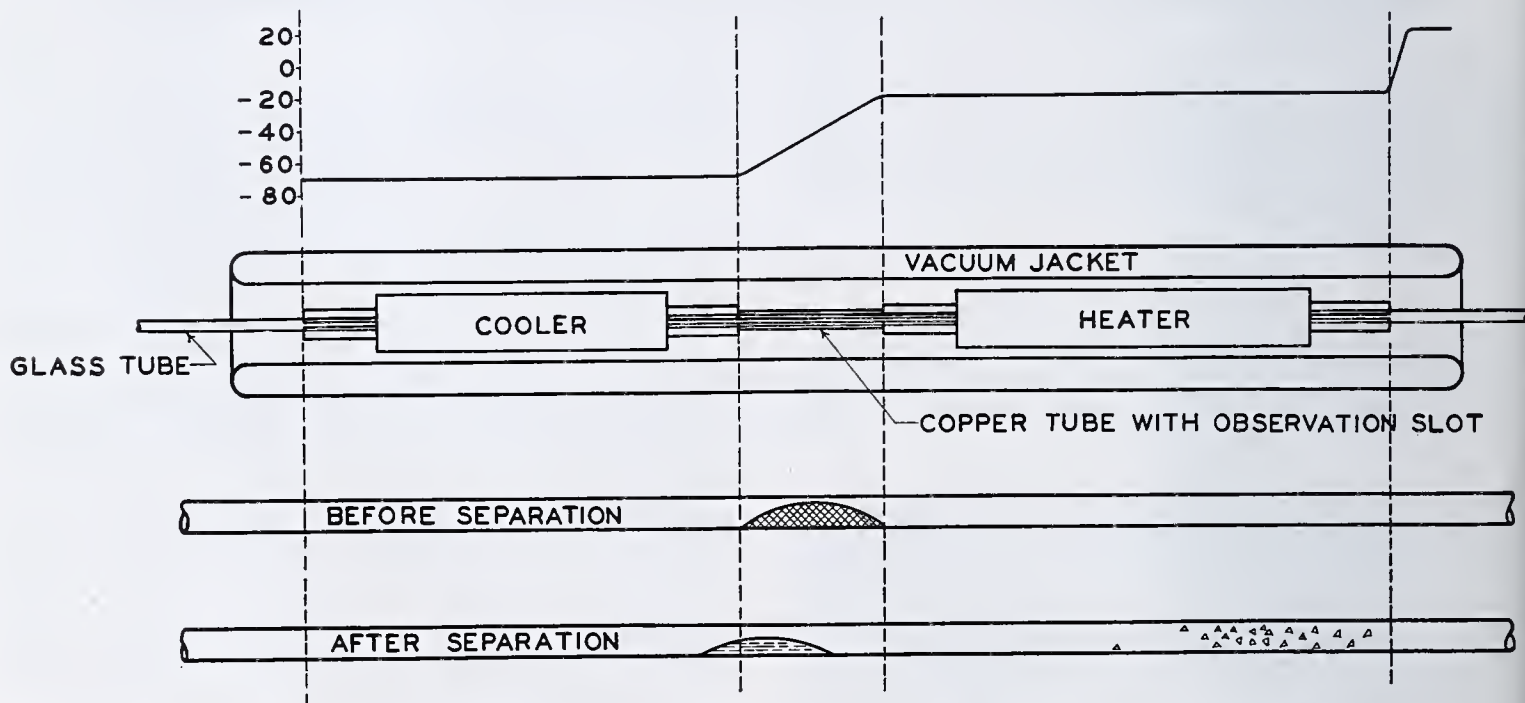


FIGURE 1. SCHEMATIC REPRESENTATION OF AN APPARATUS FOR HIGH-VACUUM FRACTIONAL DISTILLATION AS USED FOR SEPARATION OF *p*- AND *m*-XYLENES

THE usual method of fractional distillation involving gravitational reflux cannot be applied to the separation of mixtures of substances of low vapor pressure, since, to maintain a reasonably fast reflux rate, the vapor pressure of the components must, in general, exceed 1 mm. Furthermore, this method is not applicable to liquid volumes smaller than a few milliliters, since the holdup losses then become a significant fraction of the total input. With the following apparently not previously described method, which is free from

gravitational reflux, the mixture to be fractionated is placed in a rather long, evacuated glass tube, along which for a certain distance a temperature gradient is maintained by a thermostat system. The mixture tends to accumulate at the low-temperature end of the gradient, which is the coldest part of the tube; by pulling the latter slowly and uniformly through the gradient in the direction toward the warm end, the mixture can be made to distill continuously within the gradient and to separate more or less completely into its com-



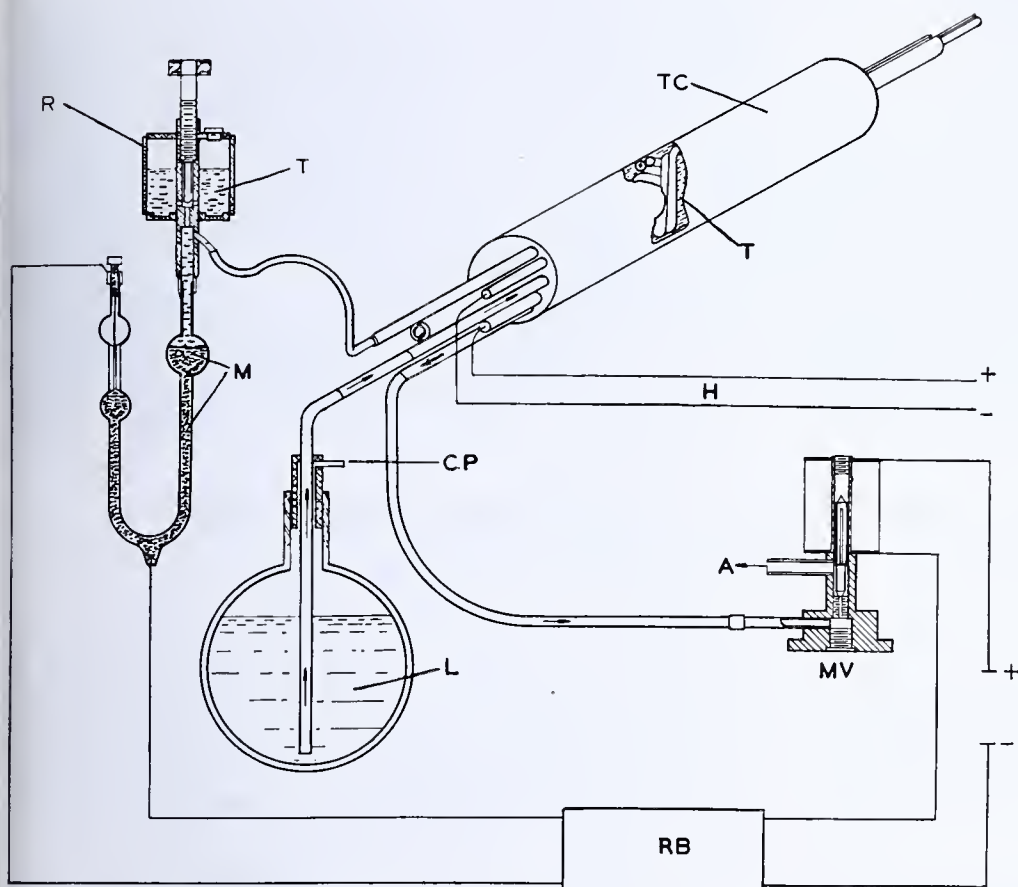


FIGURE 2. THERMOSTATIC CONTROL FOR HEATER AND COOLER

R, reservoir and regulating valve for toluene, T, by which the temperature of heater or cooler, TC, may be controlled. H, heating circuit. A constant pressure above atmospheric is maintained at CP. Liquid nitrogen, L, flows as shown by arrows on actuation of magnetic valve, MV, by mercury thermostat, M, permitting outlet of liquid nitrogen to atmosphere at A.

ponents, since the more volatile component distills faster than the less volatile. The volume of distillable substance to be used in this process can be kept very small, of the order of  $10^{-3}$  cc., and distilling temperatures corresponding to vapor pressures much below 1 mm. may be chosen.

The design of the apparatus is shown schematically in Figure 1, as used for separation of *p*- and *m*-xylenes.

The straight glass tube in which distillation takes place passed through the axial bore of two cylindrical thermostats, the heater and the cooler, and through a copper tube connecting heater and cooler. Use of a tube 4 mm. in internal diameter ensured a fairly large surface-to-volume ratio without danger of clogging, using samples up to 0.1 cc. Larger diameters were found to decrease the efficiency and ease of operation of the process. The lengths of the tubes were between 1.5 and 2 meters. The temperature gradient shown above the apparatus was maintained along the copper tube, which was 22.5 cm. (9 inches) long and had an observation slot. A transparent vacuum jacket was used to minimize heat transfer to the surroundings.

The thermostats were made entirely from copper. Their construction is shown in Figure 2. Each had two copper spirals in the inner annular spaces, one containing a heating wire, the other allowing the passage of cold air from a liquid air container. The residual annular space was filled with toluene, the thermal volume change of which operated a mercury U-tube connected to a vacuum-tube relay which was used to control either a heating current or a magnetic valve which regulated the flow of cold air, as shown in Figure 2. The temperature fluctuations did not exceed  $0.1^{\circ}$  C. Thermocouples (not shown) were arranged to permit temperature measurements at any point along the gradient. The distilling tube was clamped at one end to an electrically driven carriage which moved on rails at a uniform rate, adjustable from a few millimeters per hour to several centimeters. Provision was made, furthermore, to keep the tube constantly rotating around its axis to ensure temperature equalization over any cross section. A photograph of the entire apparatus is shown in Figure 3.

A typical case studied was the separation of *p*- and *m*-xylenes. Their boiling points at atmospheric pressure are al-

most identical,  $139^{\circ}$  and  $138^{\circ}$  C., respectively. *p*-Xylene melts at  $13.2^{\circ}$ , and below this temperature its vapor pressure is lower than that of *m*-xylene, which melts at  $-51^{\circ}$ . With the heater at temperatures below  $13.2^{\circ}$ , it was possible to follow the separation by visual observation of the crystals emerging from the liquid mixtures. Satisfactory distilling rates within the gradient were obtained if the temperature at the warm end was kept anywhere between  $0^{\circ}$  and  $-25^{\circ}$ , and at the cold end  $-50^{\circ}$  or lower.

The sample, 0.1 to 0.01 cc., was contained in a small glass tube which was placed in the distilling tube, which was then evacuated to  $< 10^{-6}$  mm. of mercury and sealed. The sample tube was then broken by thermal expansion by applying a small flame momentarily. At the beginning of the process, the volatile material was allowed to condense in the coldest zone of the tube, within the cooler. The tube was then pulled, initially, at a rate such that the substance remained within the gradient. Separation soon occurred, *p*-xylene crystals concentrating at the warm end, as shown in the tube at the bottom of Figure 1. The pulling speed was then slowly raised until the crystals left the gradient and entered the heater zone, which was 35 cm. (14 inches) long. The process was continued without further adjustment until a stationary state was reached in which the bulk of the *p*-xylene was located within the heater and the *m*-xylene, with some *p*-xylene, was distributed along the gradient. The *m*-xylene cannot be pulled from the gradient because of its faster distilling rate. With a heater temperature of about  $-15^{\circ}$ , and the cooler at about  $-70^{\circ}$ , the pulling speed was approximately 6 cm. per hour.

The pure *p*-xylene was removed by sealing off the tube at the proper place or by reducing the temperature of both heater and cooler sufficiently so that the vapor pressures became practically zero, and then pulling that part of the tube containing the *p*-xylene out of the heater and allowing it to come to room temperature, at the same time passing dry filtered air through from the cooler end. Thus the evaporating *p*-xylene was blown out and collected in a liquid air trap. The purity of the *p*-xylene separated in this way was high. The residual mixture was again

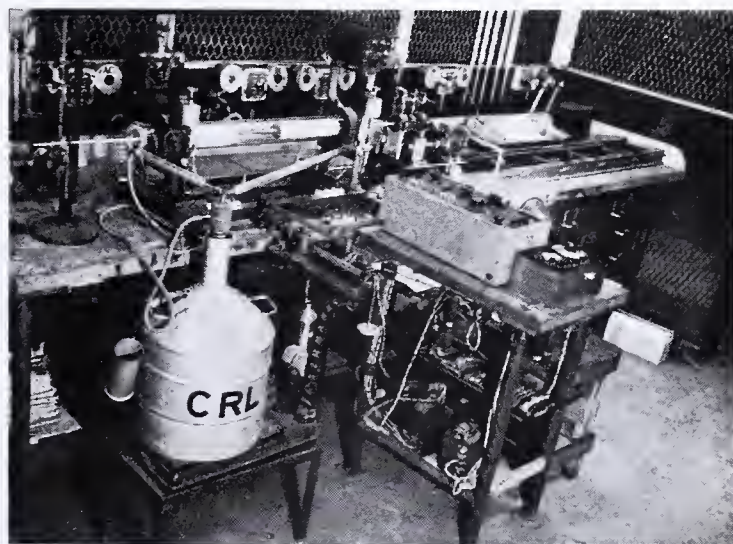


FIGURE 3. PHOTOGRAPH OF APPARATUS

Distilling tube passes through cooler and heater (left and right, respectively, within vacuum jacket) and is attached to carriage on guard rails (extreme right). In front, accessories for thermostatic control (liquid air flow regulated by magnetic valve) and thermocouple readings.



subjected to the same procedure, and an additional yield of pure *p*-xylene was obtained.

Within the distilling tube there exists a dynamic pressure gradient which tends to keep the more volatile component away from the warm end and thus favors separation of the less volatile material in the pure state. However, it also facilitates the intermixing of the vapors toward the cold end and is, therefore, the probable cause of the failure to obtain complete separation in one operation. This appears to be an

inherent shortcoming of the process which may be improved, but not completely overcome. Somewhat better separation was obtained in packed tubes, but other disadvantages arose; the distilling rate was slowed down and the visual observation was hampered. In principle, it does not seem impossible to obtain pure fractions of the more volatile components, although in our experiments the more volatile component generally contained a few per cent of the less volatile component.

RECEIVED December 18, 1937.

## A Simple Method for Preparing Glass Electrodes

M. L. NICHOLS AND JOHN M. SCHEMPF, Cornell University, Ithaca, N. Y.

WHILE investigating the problem of making a glass electrode with a sufficiently low resistance ( $10^4$  to  $10^5$  ohms) to permit its use with an ordinary galvanometer and potentiometer (1), the following procedure was evolved. This method was found to be easy to carry out, and yielded a sturdy product of high sensitivity.

Using 9-mm. Corning 015 glass, the parts shown in Figure 1, A, B, C, are prepared. A is formed by breaking off about half of a thin bulb blown on a section of 2- to 3-mm. tubing drawn from the 9-mm. stock. B is a short piece of 9-mm. tubing with an attached spindle to serve as a handle, and C is a section of the original tubing 10 to 12 cm. long.

To prepare the electrode, B is heated to softening at the open end and attached lightly to A, following which C is heated and sealed to B, over A, as shown in D and E. The seal is then heated uniformly and gently blown out to give F. The excess glass is cut off by a hot wire at the positions indicated by the dotted lines in F.

If the electrode is sufficiently sensitive, a spot of interference figures 9 to 16 sq. mm. in area will appear in the diaphragm.

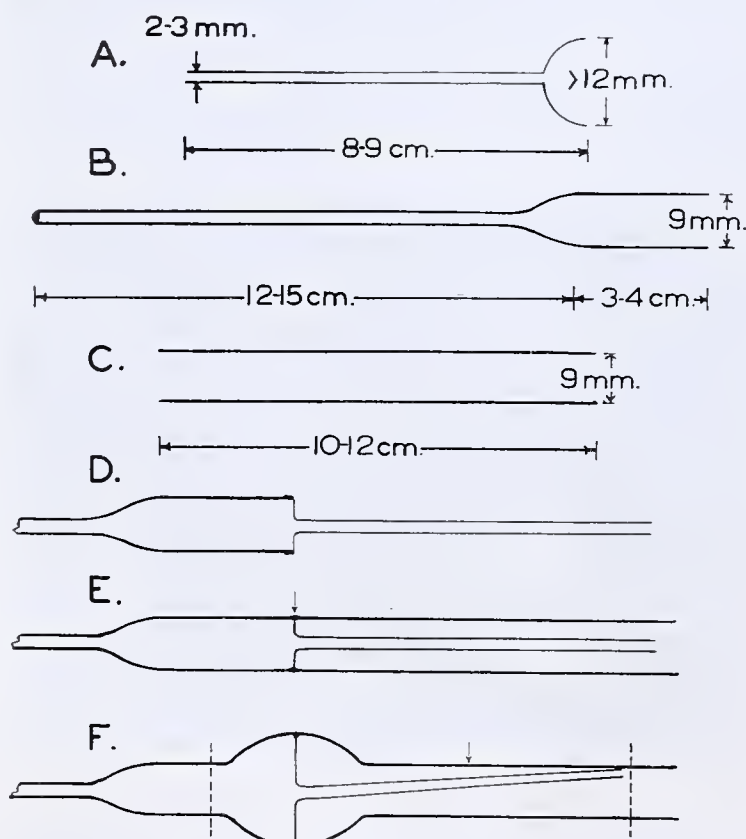


FIGURE 1. PREPARATION OF ELECTRODE

The thickness of the bulb blown in preparing A controls the diaphragm thickness for any final electrode size. It is not important or usually possible for the capillary to remain in the center of the diaphragm. The electrode is ready for use after a preliminary soaking in approximately 0.1 *N* hydrochloric acid for at least 36 hours.

As used in this laboratory, the electrode is rinsed with distilled water, superficially dried with filter paper, and filled to the level indicated by the arrow in F with a saturated solution of quinhydrone in approximately 0.1 *N* hydrochloric acid. A bare platinum wire is then inserted to make electrical contact. A convenient assembly is shown in Figure 2. The asymmetry potential which always develops across the diaphragm is determined on a solution of known pH value.

The precision obtained with this electrode used in conjunction with a Leeds & Northrup enclosed lamp and scale galvanometer and a potentiometer reading to 0.1 millivolt is better than 1 millivolt or 0.02 pH unit.

The advantages of this electrode are its mechanical stability, sensitivity (permitting its use with apparatus usually available), and ease of manufacture.

Obviously, this type of construction can be modified to suit individual requirements.

### Summary

A simple procedure for making a very sensitive, durable glass electrode is given. Accurate measurements may be made with this electrode using a portable galvanometer with a sensitivity of the order of 40 megohms and an ordinary galvanometer.

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RECEIVED February 28, 1938.

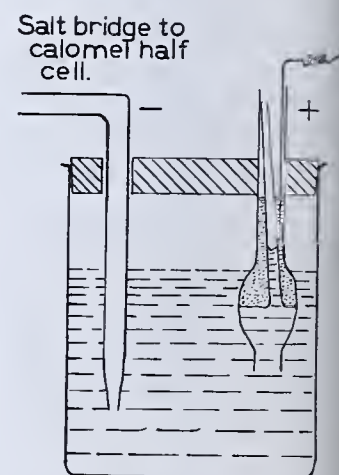


FIGURE 2. ELECTRODE ASSEMBLY





**Modern**

**Laboratories**

## New Laboratories of the Bureau of Mines Petroleum Experiment Station

HAROLD M. SMITH, Petroleum Experiment Station, Bartlesville, Okla.

THE United States Department of the Interior research activities on petroleum and natural gas are centered at the Bureau of Mines Petroleum Experiment Station at Bartlesville, Okla., where there has been established one of the largest and best-equipped public institutions in the world devoted exclusively to the study of the problems and difficulties confronting the petroleum and natural gas industry. The station's work may be classified under the general heading of: (1) problems in the production of petroleum and natural gas, including related problems of pipe-line transportation; (2) engineering field studies of typical oil and gas fields; (3) chemistry and refining of petroleum; and (4) special technical studies, such as losses by evaporation, corrosion of oil and gas-field equipment, methods of "shutting in" oil and gas wells to prevent damage during periods of inactivity, disposal of oil-field brines, and the general subject of safety in oil fields and refineries.

The general and routine work includes crude oil distillation analyses, lamp and bomb sulfur determinations, water analyses, viscosity and specific gravity determinations, porosity and permeability determinations on oil-sand cores, gas analyses, and miscellaneous tests of a more or less standardized nature. Some of the present research activities include separation of petroleum into small fractions; determination of the physical and chemical properties of these fractions, in-

cluding detailed studies on certain properties; removal of occluded salt in crude oil; corrosion studies; natural gas solubilities; pressure-volume-temperature relationships; and related problems pertaining to the chemistry and physics of petroleum. This abstract of the activities of the station shows at once the need for laboratory facilities that are widely different from those found in the usual university or industrial laboratory.

An opportunity to design and equip laboratories in keeping with the needs of the institution occurred in 1935 when the Public Works Administration allotted funds for a laboratory and office building. This article presents the more important features of construction and equipment. To a large extent these features represent the combined ideas and efforts of the laboratory staff. Architectural requirements were found to be a restricting force in some instances, but on the whole the plans and descriptions given below constitute the fulfillment of the laboratory worker's ideas to a degree not generally found.

Properly planned laboratories should have, among other things, a minimum number of places where dirt and dust can collect; noncorrosive hardware and fixtures; adequate services and outlets; easily cleaned, well lighted hoods; suitable general illumination; easily cleaned, durable walls and floors; and safe construction and equipment.



NEW BUREAU OF MINES PETROLEUM EXPERIMENT STATION

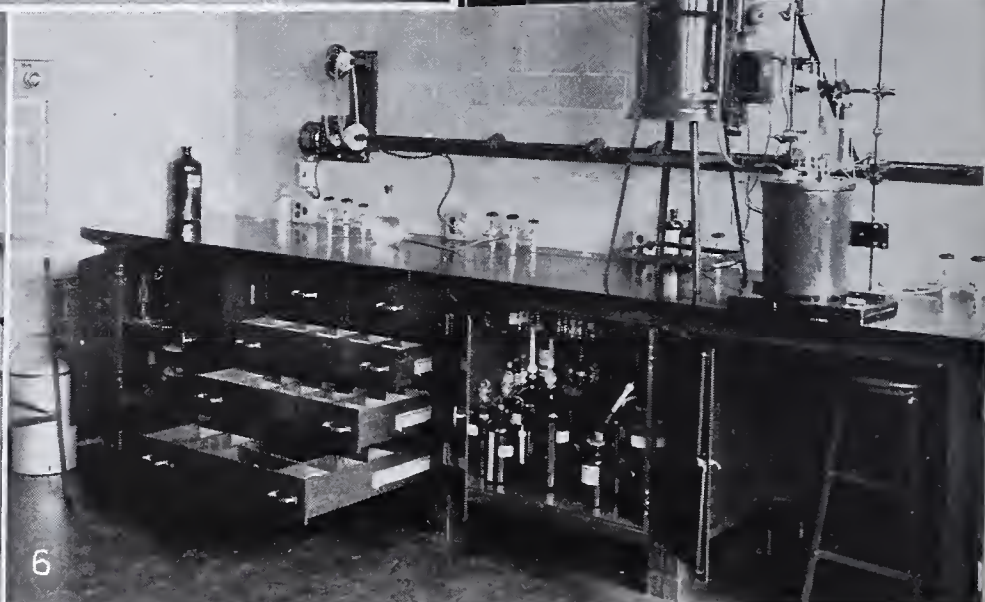
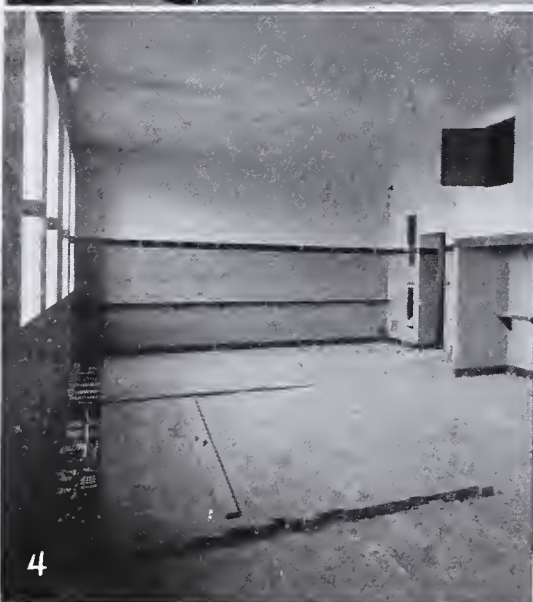
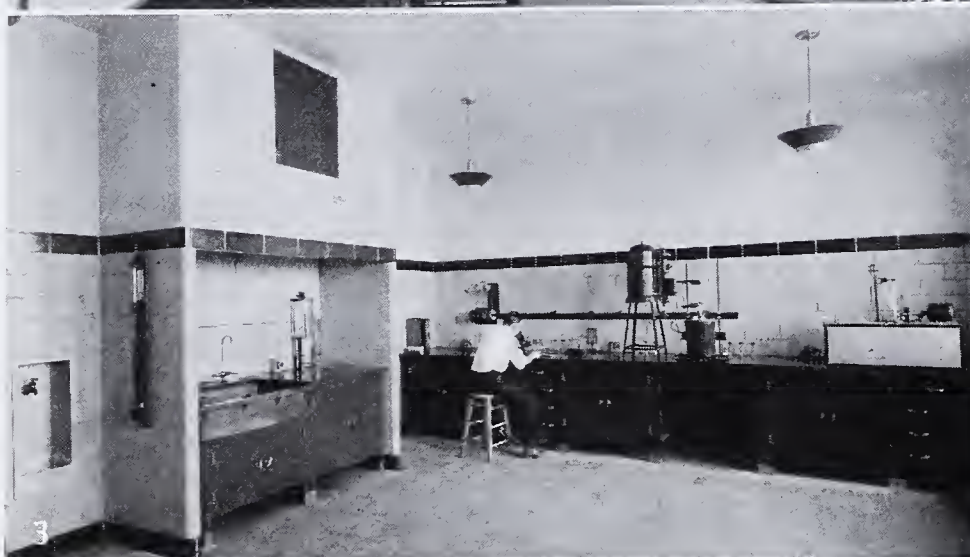


The possibility of fire and explosion can be lessened by proper attention to venting of all pipe-chases in both walls and floors; using a color code for easy and positive determination of service lines; suitably located easily worked shut-off valves; regular testing of high-pressure equipment, such as

gas storage cylinders; using a color code to distinguish the several gases; adherence to code requirements in electrical installations; and taking precautionary measures for the storage of easily inflammable material. In case of fire there should be readily available fire extinguishers in working condition, quick-acting showers or fire blankets, and suitable alarm devices. Injury due to mechanical causes can be minimized by providing adequate lighting, especially in hoods, halls, and stairways and at machines; by suitable guards for belts and other moving machinery; by removing obstructions in passageways, and by suitable location and construction of doors. First-aid equipment in usable condition should be readily available, and each laboratory should have posted conspicuously information as to the location of master switches and valves.

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1. TRANSITE PIPE HOOD DUCTS
2. SECTION OF WORKSHOP
3. SECTION OF RESEARCH LABORATORY
4. WOOD-BLOCK FLOORING AND SERVICE SHELVES
5. SECTION OF GENERAL LABORATORY
6. DETAILS OF DESK CONSTRUCTION





Laboratory Arrangement

The laboratories occupy the second and third stories of the center section of the new building. The general construction of both stories is identical, but the second story is largely planned for general laboratory work, and the third story for research. The floor plans show the layout of the rooms and their approximate size. Several photographs of various parts of the laboratories are included in this article.

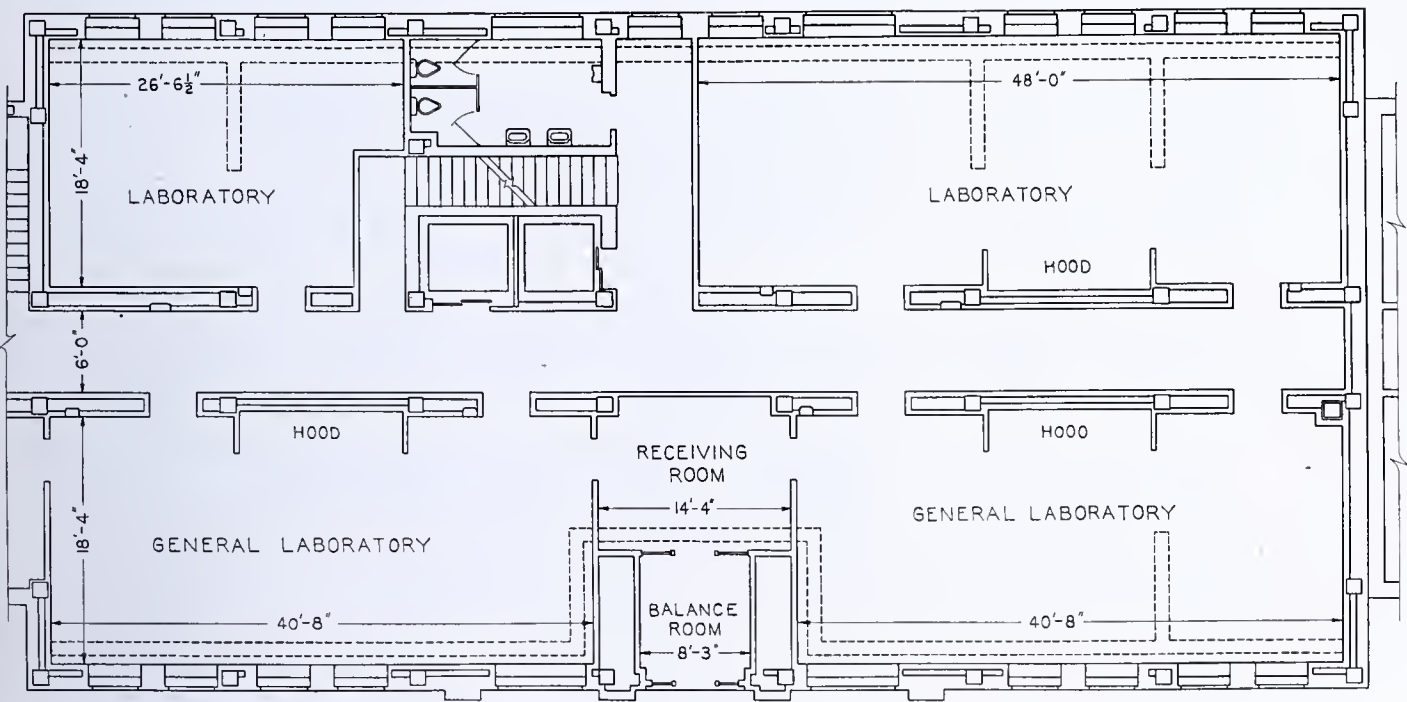
Laboratory Construction and Equipment

**FLOORS.** The floors are of Douglas fir blocks 2 × 4 inches in cross section and 3.75 inches thick, set with the end grain up on a reinforced concrete floor coated with asphalt. The blocks are locked together near the base with wooden splines. These wooden floors do not fatigue the feet of the laboratory worker and after several oilings are dark brown and blend well with the laboratory finish. They also are easily kept clean.

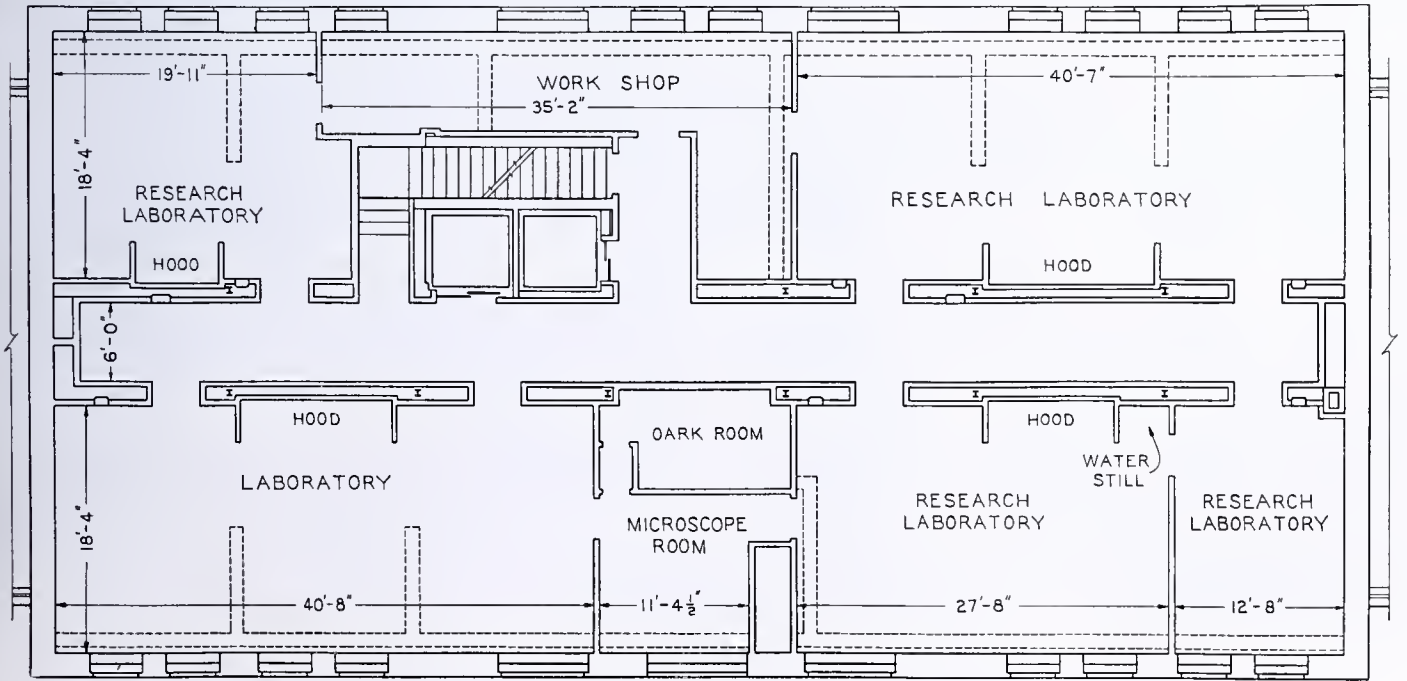
**WALLS.** The walls up to a height of 6.5 feet are cream "enamel"-finish hollow tile, 5 × 12 inch face. The upper part of

the walls is cement plaster on wire lath or on gypsum blocks and is finished with light-cream laboratory paint. The ceilings are cement plaster coated with white laboratory paint. A band of dark-brown tile is used at the base of the wall, and makes a square corner with the floor so that equipment may be pushed flush with the wall. Another dark band is used at the top of the tile. At certain intervals in the walls 0.25-inch steel plates 5 × 12 inches have been bolted and grouted into the walls so that equipment may be fastened to the wall without drilling the tile. Where it is necessary to drill the tile, Rawl plugs for holding the screws have been found satisfactory. In most cases it is possible to drill the mortar between the tile, but the tile itself may be drilled if necessary, as for the service shelves, and toggle bolts used. Small star drills are satisfactory for this purpose.

**Hoods.** Hoods are built in and constructed of enamel tile to a height of 8 feet 6 inches on the rear and sides, while the top of the front opening is 6 feet from the floor. A reinforced-concrete platform is carried on the tile end walls and on it are mounted the hood fans. The fans (300 cubic feet per minute capacity) are direct-connected to 0.5 horsepower, 3-phase, 220-volt motors. A good idea of the arrangement and general construction may be obtained from the cross section plan. The hoods are on the

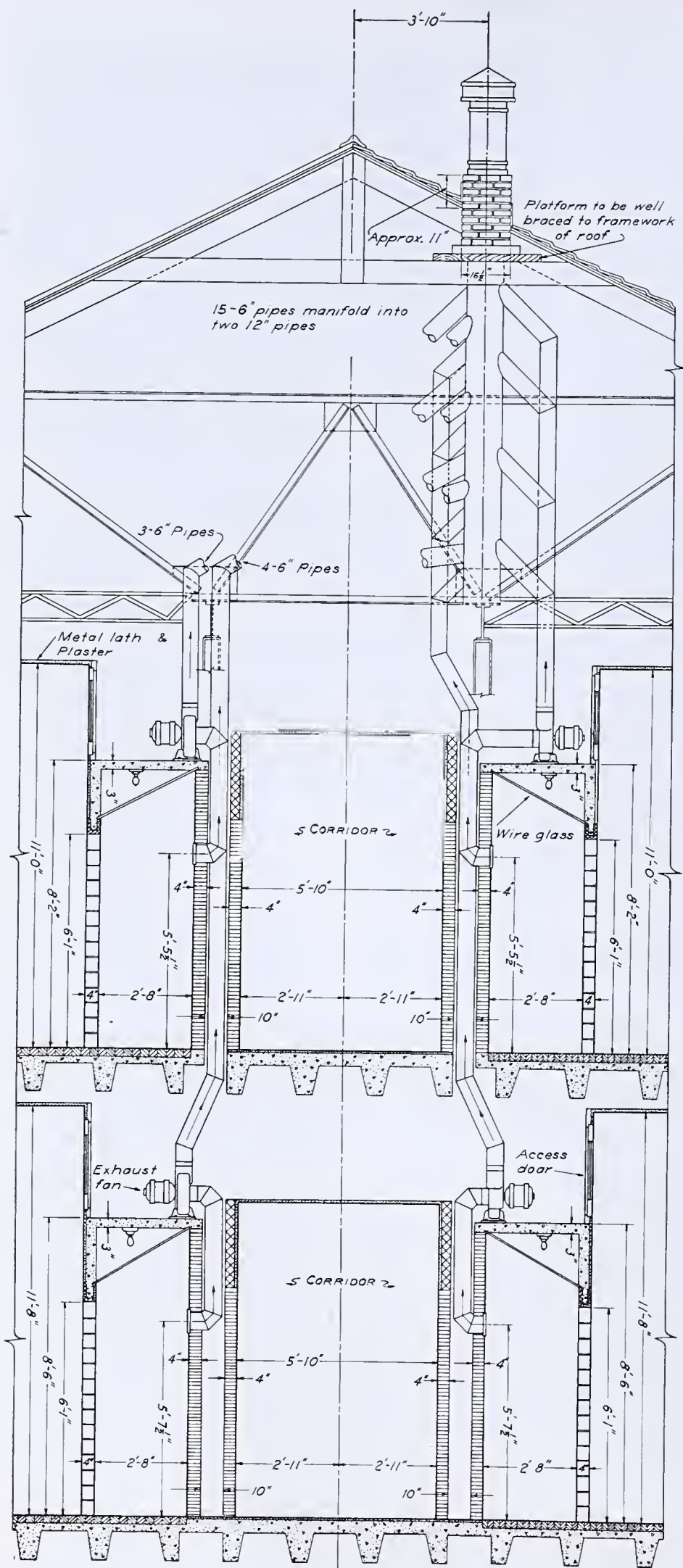


SECOND FLOOR PLAN



THIRD FLOOR PLAN





CROSS SECTION OF HOODS

corridor walls, which are rather thick to accommodate air-conditioning ducts, and where possible the hoods have been set back in the wall, thus saving some laboratory space. The hoods are vented through 6-inch Transite pipes concealed in the walls to 12-inch manifolds which pass through the roof. One fan is used for every 3 linear feet of desk space in the hood, and when the desks are in place there are approximately 9 square feet of opening for each fan. Each hood is baffled on the inside with 0.25-inch sheet Transite mounted on aluminum channel in such a way that the draft is distributed between the top and bottom of the fume space. Arrangements are also provided whereby Transite partitions may be inserted every 3 feet, thus dividing a long hood into sections if desired. Lights are provided on the under side of the concrete top and shielded with clear wire glass set at an angle of about 30°, sloping upward from the front. Switches for both lights and fans are situated in the end walls of the hoods. These fan switches operate magnetic switches for starting the 3-phase motors.

**PIPE TRENCHES.** Pipe trenches run the full length of the laboratory floor space along the outside walls of the second and third floors, passing under the partitions, so that piping or any special tubing for experimental work may be run from one room to another as desired. At certain intervals in the room where permanent benches are not contemplated, trenches have been run about 9 feet towards the center of the room. Service lines may be brought out in these trenches for use with apparatus away from the walls.

**SERVICE SHELVES.** Along the walls where laboratory desks are to be used ebony-asbestos service shelves are installed. These are 1.5 inches thick and 6 inches wide supported on brackets attached directly to the tile wall. These service shelves are flush with the top of the desk when it is in place and carry all the services—that is, cold water, air, gas, 110- and 220-volt current, and waste. No service lines are attached to the desks. In order to make full use of this method of piping the services, it was necessary to design laboratory furniture to fit the situation as described below.

**WATER, AIR, AND GAS LINES.** Cold water, air, and gas are brought to each laboratory direct from the mains in the basement, or in the case of large laboratories to two different positions in the laboratory. They are then piped along the walls where the desks are to be placed, and fastened on iron hangers which are in turn supported by the service shelves. Copper pipe has been used throughout. Every 3 feet service risers are brought up through holes in the service shelves and terminate in angle valves. Three-eighth-inch chromium-plated valves have been used, with metal seats for air and gas and renewable seats for water. Special 0.375 × 0.25 inch hose-attachment nipples screw into these valves. Each bench has an individual cut-off for each service line. In addition there are cut-off valves in the basement for the various laboratories.

**WASTE LINES.** On the service shelves waste outlets (chromium-plated plugs with 1-inch outside diameter tail-pieces) which fit flush to the shelf are used. Each waste outlet makes a slip joint beneath the service shelves with a galvanized 1-inch line that connects to a Monel trap at the end of the bench. The Monel traps connect to cast-iron vertical soil lines in the walls. These lead to the basement, and connect with horizontal lines that manifold into a large stoneware trap beneath the surface of the ground outside the building. Vent



lines are carried into the attic, manifolded together, and finally vented through the roof.

**ELECTRIC CONDUITS AND LINES.** Each laboratory is supplied with 110- and 220-volt single-phase alternating current service. Individual mains are brought direct from the main switchboard in the basement to a switchboard beside each laboratory doorway. In this switchboard is a main switch that cuts off power in the whole room or, in the case of a large room, a section of it. The switchboard also contains automatic cut-outs that open at 25-ampere load and are manually reset. No fuses are used. From the switchboard separate conduits run within the walls to each desk location, coming out just below the service shelves. This conduit is carried along the wall just above the waste line and at 3-foot intervals risers pass through the service shelf to cast-aluminum boxes, each of which contains two 110-volt receptacles and one 220-volt receptacle. In addition to the outlets on the benches, outlets are also provided at convenient locations in the laboratory walls, and special receptacle boxes may be used.

**SINKS.** The sinks are designed to fit in with the desk assembly and have special 10-inch service shelves back of them which carry service outlets for both hot and cold water. The sinks are of acid-proof stoneware with either a left-hand or right-hand drain board or both, depending upon the location. When this type of sink is used care should be exercised to see that well-processed even units are provided by the manufacturer.

### Distilled Water

Because of the hardness of the available tap water, a system using cistern water for the production of distilled water has been installed.

The cistern water is fed from a supply tank, 1, through a pump, 2, into a 2-horsepower water-tube boiler, 3, at 60 pounds' pressure. The steam from this boiler is divided at point 4: part of it passes through the steam coil, 5, of a Barnstead still, 6, and then returns to the boiler; the other portion of the steam is condensed, 7, 8, and is redistilled in the Barnstead still. The boiler and still are on the third floor, and the vapor line from the Barnstead still, 9, passes through the ceiling into the attic, where the vapor is condensed, 10, and the final distilled water collects in an aluminum tank of 100 gallons' capacity, 11. From there it is piped to the various laboratories through aluminum pipe and Monel bibs. The entire operation is automatic once it has been started. Provision is made for draining both still and boiler. The distilled-water outlets in reality are small sinks about 12 inches wide, 8 inches deep, and 30 inches tall of cast aluminum set vertically in the wall. At the bottom of each sink is a connection to waste, and a 3-inch lip at the bottom prevents water from running out into the room. By this arrangement distilled water may be easily run to flasks, beakers, and cylinders without dripping to the floors.

### Safety and Miscellaneous Features

The laboratories are of entirely fireproof construction, with the exception of the floors. However, since these are a solid mass on concrete they will not burn readily. All doors and door casings are steel with grained walnut finish, and window casings are also steel with brown finish. At present some of the door panels are steel or frosted glass and some clear wire plate glass. As a safety measure to avoid striking people when doors are opened suddenly, it is planned to replace all steel panels with clear wire plate glass.

A 1-quart carbon dioxide-type fire extinguisher has been placed in each laboratory doorway leading to the corridors. In the corridors between the laboratories, showers have been installed about every 20 feet, each operated by a pull chain hanging within convenient reach of anyone traversing the hallway. These are for emergency use if the laboratory worker should catch fire or have a serious accident with chemicals. There is a drain in the floor under each shower.

All the general lighting in the laboratories is semi-indirect with one 300-watt lamp to about every 80 square feet of ceiling area. Good illumination not only saves the eyes of the laboratory worker but helps to prevent accidents.

One room has been set aside as a workshop for the use of the research workers only and contains a glass-blowing bench, glass tubing cabinet, vacuum pump and gage, drill press,

grinder, small (3.5 feet by 9 inch) lathe, tool chest, and soldering bench. In addition, supplies such as bolts, screws, pipe fittings, paint, and wire are stored here. This room makes it possible for the research worker to make and repair his apparatus outside of the actual laboratory and under better conditions. This in turn keeps the laboratory cleaner and helps to eliminate accidents due to the close proximity of pipe wrenches to glass apparatus.

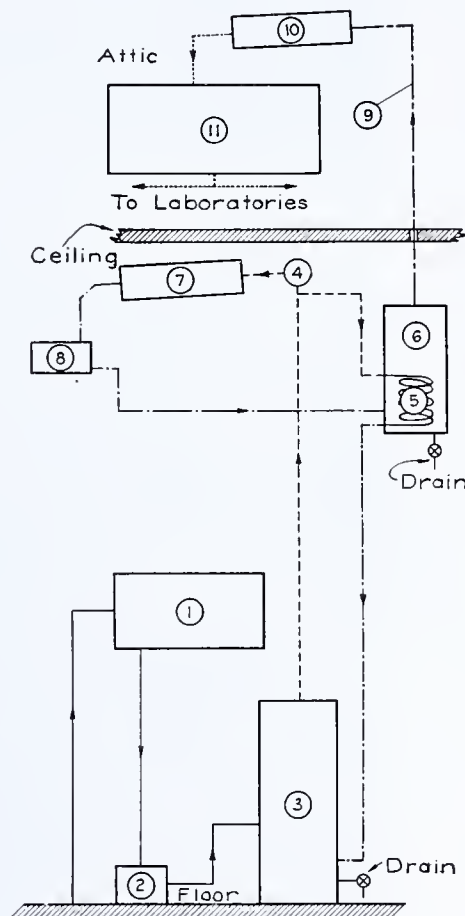


DIAGRAM OF DISTILLED WATER SYSTEM

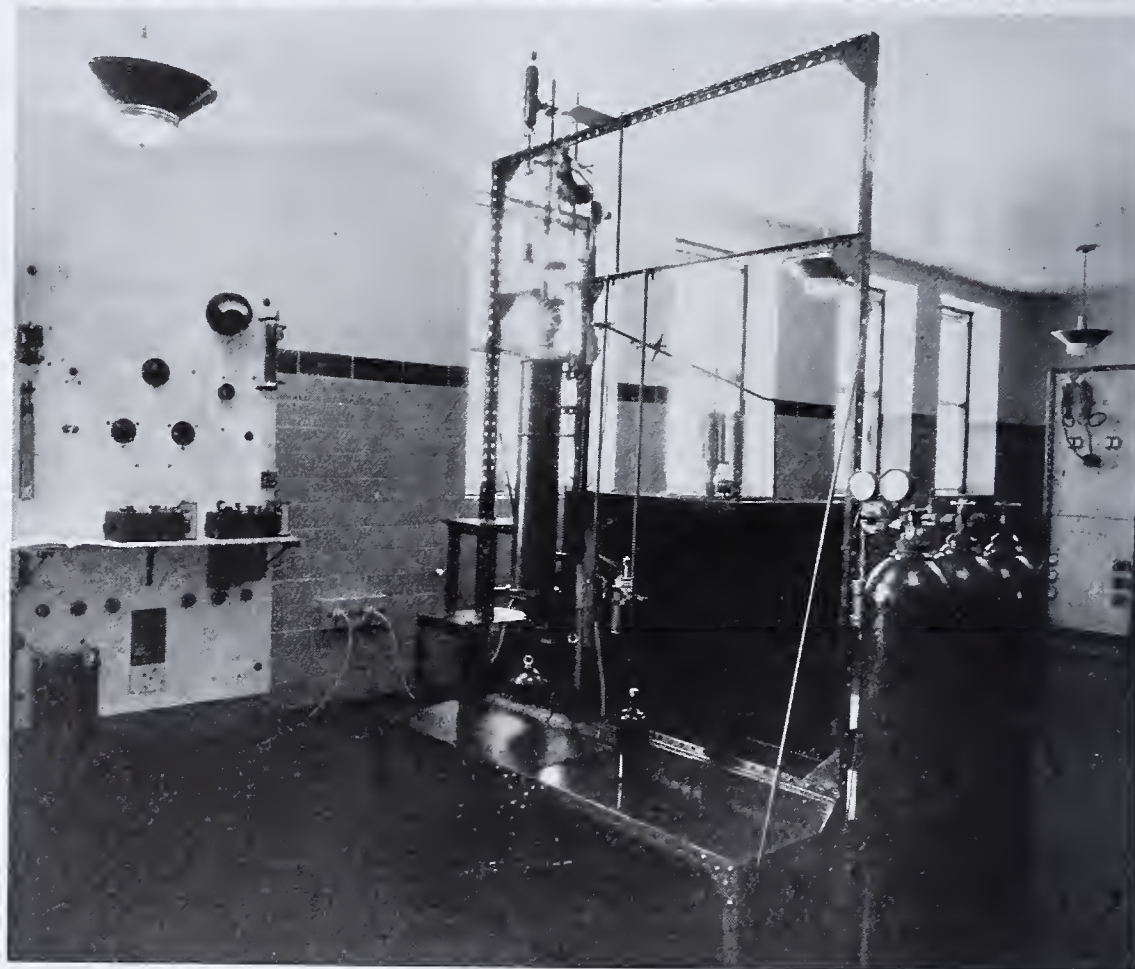
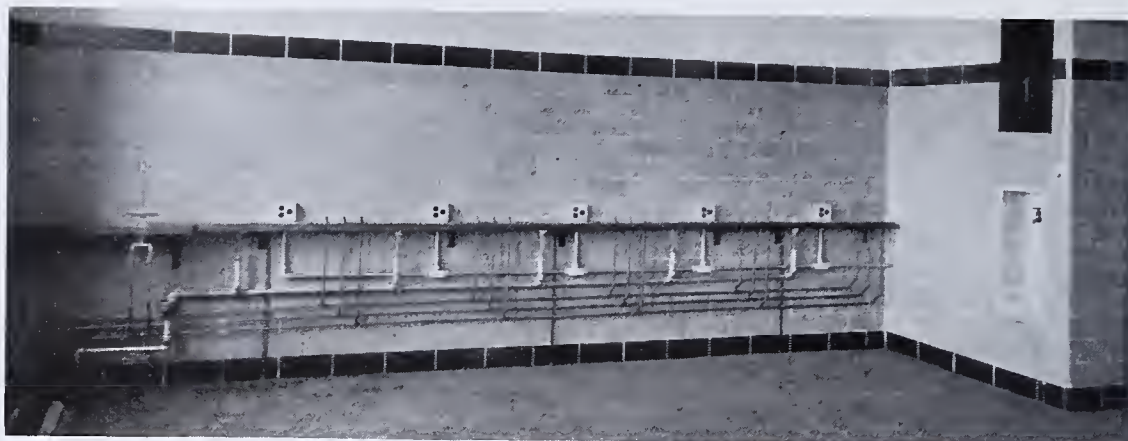
- |                                |                               |
|--------------------------------|-------------------------------|
| 1. Boiler supply tank          | 9. Vapor line                 |
| 2. Pump                        | 10. Distilled water condenser |
| 3. Boiler                      | 11. Distilled water tank      |
| 4. Valve                       | — Cistern water               |
| 5. Steam coil                  | — Steam from boiler           |
| 6. Barnstead still             | — Condensed boiler steam      |
| 7. Condenser                   | — Barnstead still vapor line  |
| 8. Barnstead still supply tank | — Distilled water             |

All the laboratories are heated and cooled by forced air circulation. When such a system is used in laboratories dampers should be placed in the returns so that obnoxious and dangerous fumes, if released in one room, will not permeate the building.

### Laboratory Furniture

The laboratory desks are interchangeable steel units designed by the members of the station. There are three kinds of desk units, the cupboard, drawer, and open type. Each unit is 36 inches wide, 34.5 inches high, and 26 inches deep. Adjustment bolts in the legs provide for small variations in height. All units are lead-coated and finished in dark olive-green acid- and alkali-proof enamel. Tops are of ebony asbestos 1.5 inches thick and 28 inches deep, and generally either 38 or 74 inches long. This provides tops for 1, 2, 3, or 4 units with a 2-inch overhang at the ends. When the desk units and tops are in place there is a working surface 36 inches from the floor and 34 inches deep. This is deeper than most laboratory desks, but the increased space is very useful and service outlets may still be easily reached.





*Upper.* SERVICE LINES  
*Lower.* ANGLE-IRON SUPPORT UNIT

One of the greatest aids to an orderly laboratory is a place to keep small items. To assist in this the drawers were made with slots on all sides, and partitions can be made at the laboratory or tin shop that will provide many bins for clamps, thermometers, corks, etc. In the cupboard units shelves of two different widths, adjustable on 0.5-inch centers, are provided. The open unit makes an available storage space for stools when they are not in use.

Balance cases and tables are also of steel construction with enamel finish. The tables have linoleum tops, and the cases are of the sliding-door type. Although no special feet have been provided, there is no vibration so long as the tables do not touch the walls.

Sinks are mounted on steel cabinets that harmonize with the other units and have doors in front that permit access to the trap and also to storage spaces.

For equipment that does not fit well on desks, such as gas-analysis and distillation apparatus, special units of punched angle iron have been designed. To these may be bolted angle-iron frames of desired size and shape. One-quarter-

inch iron pipe and lock nuts provide rods where needed, and also are used for braces. Several layers of plywood with a 0.25-inch ebony-asbestos top make a satisfactory table top for these units.

### Acknowledgments

The design and construction of these laboratories necessarily contain the ideas of many men, and to all who contributed the author acknowledges his indebtedness. To one man, N. A. C. Smith, supervising engineer of the station, we owe a great deal, not only for his suggestions but also for his encouragement and coöperation in the development of new ideas of various members of the staff. Many of the unusual and different features are due to Harry T. Rall, and his help is gratefully acknowledged. The book entitled "The Construction and Equipment of Chemical Laboratories" by the National Research Council was also of considerable value.

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# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## The Technic of Antifreeze Testing

KENNETH H. HOOVER AND FRANK E. DOLIAN

Commercial Solvents Corporation, Terre Haute, Ind.

The suitability of an antifreeze solution for use in a water-cooled internal-combustion engine is determined by the inherent properties—i. e., physical constants—of its principal component and by the properties imparted to it by the addition of certain modifying agents. The technic of testing the corrosive action on metals, storage properties, attack of rubber, and foaming tendency is discussed, and various apparatus are described. Particular emphasis is placed on methods of testing corrosive action which closely simulate actual conditions as found in automobile cooling systems. Field tests and their limitations are discussed.

THE commonly available antifreeze solutions for use in water-cooled internal-combustion engines are generally divided into two classes, known as volatile and nonvolatile "permanent" types. All the preferred materials are alcohols, such as methanol, ethyl alcohol, ethylene glycol, and glycerol. Both trimethylene glycol and propylene glycol could also be satisfactory materials.

The suitability of an antifreeze is determined by the inherent properties of its principal component, and by the properties imparted to it by the addition of certain modifying agents. Inherent properties are physical constants and cannot be changed to any appreciable extent. Properties such as corrosive action on metals, attack of rubber, foaming tendency, etc., can be changed or modified, however, and, from a technical viewpoint, provide the only means of attaining competitive superiority. It is with these properties, therefore, that the evaluation of antifreeze solutions is chiefly concerned, and this paper will deal with the technic of testing these "imparted" properties of antifreeze solutions.

### Corrosive Action on Metals

In the cooling system of an automobile engine, there are several different metals and alloys in contact with the cooling liquid. These metals or alloys are chiefly copper, brass, iron, steel, and sometimes aluminum (about one-fourth of the 1938 models are equipped with aluminum cylinder heads).

These metals are not only in contact with the cooling liquid, but are also in contact with each other in most cases, making an ideal situation for electrochemical corrosion. To make the conditions even more ideal for corrosion, nearly every cooling system is subject to a certain amount of aeration because of leaks in the cooling system on the low-pressure or intake side of the water pump. These leaks may not be of sufficient size to allow liquid to escape, but may be large enough to allow air to enter when the pump is running, and there is a positive external pressure on this part of the system. Aeration also occurs in the upper tank of the radiator.

The part played by oxygen in the mechanism of corrosion is well known. According to Speller (2), appreciable corrosion can take place only if the polarizing film of hydrogen atoms produced by the reaction of the metal with hydrogen ions in the solution is continuously removed by some means. This film of atomic hydrogen can be removed either by combining to form molecules of hydrogen which are released as gas, or by reaction with dissolved oxygen to form water. In either case, the continuous destruction of the hydrogen film allows the metal to go into solution and corrosion proceeds at a rapid rate. In neutral, or slightly alkaline, solutions, which are usually dealt with in working with antifreeze solutions, the amount of gaseous hydrogen is very small compared to the amount of hydrogen destroyed by oxidation. Not only dissolved oxygen plays a part in corrosion, but also mechanically entrained air is stated by certain investigators (1) to increase the rate of corrosion of brass. Therefore, in testing the corrosive properties of an antifreeze solution, there must be electrolytic couples and aeration if it is wished to simulate actual operating conditions. Much stress is placed here on these two factors because they are too often overlooked in testing.

The problem of corrosion by antifreeze solutions is considerably more complicated than most corrosion problems, both in the matter of testing and in the matter of protecting against corrosion. In the ordinary corrosion problem, only one metal is concerned, while in an automobile cooling system, there are at least four metals, comprising at least five elements, which must be protected simultaneously against corrosion by the addition of suitable inhibitors.

There are very few, if any, single inhibitors which protect all of the metals found in a cooling system. It is a comparatively simple matter, for instance, to find a material which will inhibit the corrosion of iron. Frequently, however, such an inhibitor for iron is harmful to one or more of the other metals. Hence, it becomes necessary to add an "inhibitor to inhibit an inhibitor" and the only way to get complete pro-



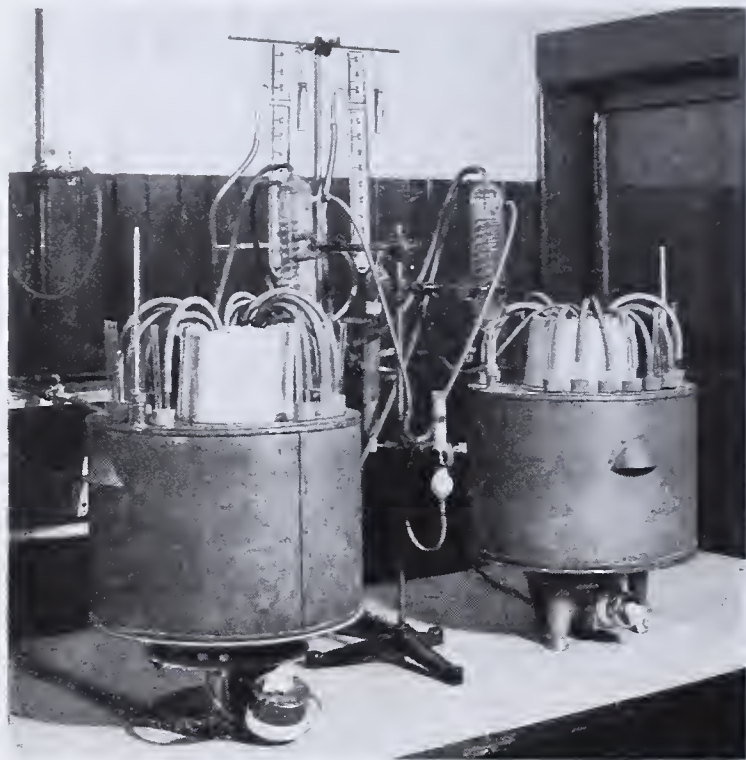


FIGURE 1. APPARATUS FOR PRELIMINARY CORROSION TESTS

tection of all metals is by the use of a combination of inhibitors.

In any case, the only way to obtain complete protection is by use of various combinations of inhibitors. In developing a satisfactory inhibiting combination, therefore, an enormous number of combinations must be tested, unless the experimenter is fortunate enough to find the right one early in his investigation. It is necessary for this reason to employ small scale testing equipment in which large numbers of preliminary tests can be made simultaneously, with consequent economies of time and money, thereby eliminating unsatisfactory combinations and singling out promising combinations for more extensive study in larger scale equipment.

The authors have found the equipment shown in Figure 1 very satisfactory for preliminary corrosion studies of antifreeze solutions.

A copper bath containing a suitable liquid refluxing at the temperature at which it is desired to make the tests serves as a constant-temperature bath. Each bath contains twenty-four wells, arranged around the edge in circular fashion, each of size to hold a  $25 \times 200$  mm. test tube, and a large well in the center of size to accommodate a 0.946-liter (1-quart) wide-mouthed fruit jar. This jar serves both as an air distributor and as an air saturator. In testing antifreezes, provision must be made to minimize evaporation losses and consequent changes in concentration incurred by aeration in the test tubes containing the experimental antifreezes. The air is therefore passed through an antifreeze solution of the same concentration in the large center jar as is used in the corrosion tests, and is distributed through twenty-four holes in the specially constructed lid (Figure 2). A length of capillary tubing inserted in the rubber tubing running from each hole in the lid to each test tube meters the air, so that when twenty-four capillaries are used which deliver the same amount of air under the same pressure, the air flow to each tube is the same and can be controlled by varying the air pressure in the center jar. An air flow of approximately 5 cc. per minute to each tube is used. The air pressure in the jar is measured by a manometer and is kept constant by a suitable type of mercury regulator.

The tests are carried out in duplicate in  $25 \times 200$  mm. test tubes, using in each tube 55 cc. of an antifreeze solution freezing at  $-20^\circ$  F. This concentration was chosen merely because it happens to be a common degree of protection in actual midwinter use of antifreeze. Deep well water of fairly constant hardness (about 17 to 22 grains per gallon) is used in preparing the solutions. Test pieces of soft steel, brass, and solder,  $11.43 \times 1.27$

$\times 0.08$  cm. ( $4.5 \times 0.5 \times 0.031$  inch) with a 0.48-cm. (0.188-inch) hole near one end, are ordinarily used, although other combinations, of course, may be employed. The three strips are fastened together at one end with a small brass bolt, using brass washers as spacers between the strips. In some cases, an aluminum test strip is also used, but this tends to make a crowded arrangement, and is not generally necessary in preliminary tests. Soft steel and brass have been found to behave very much like cast iron and copper, respectively, in regard to corrosion by antifreeze solutions. The extent of corrosion differs somewhat, but any solution which attacks soft steel will also attack cast iron (3), and most solutions which attack copper will also attack brass. Hence, soft steel is used in place of cast iron as a matter of convenience in making the test pieces.

In addition to the test pieces, 1 gram of steel wool is placed in each tube to provide a large iron surface such as is found in an automobile cooling system. The arrangement of the contents of each tube should be uniform, so as to preclude the possibility of errors creeping in due to changes in the relative positions of the test pieces, the steel wool, or the glass tube which discharges the air at the bottom of the test tube. Further reduction in evaporation losses is accomplished by fitting each tube with a 10-cm. (4-inch) air reflux condenser made of glass tubing (Figure 2, right).

In preparation for the tests, the metal specimens are first brightened on a steel brush buffer, then numbered with a metal stamping tool. They are washed with soap and water using a stiff brush, rinsed in clear water, and dried with a clean cloth. They are then immersed for a few minutes in a 50-50 mixture of toluene and ethyl acetate, carefully wiped dry with a clean soft cloth, and placed in a desiccator to await weighing.

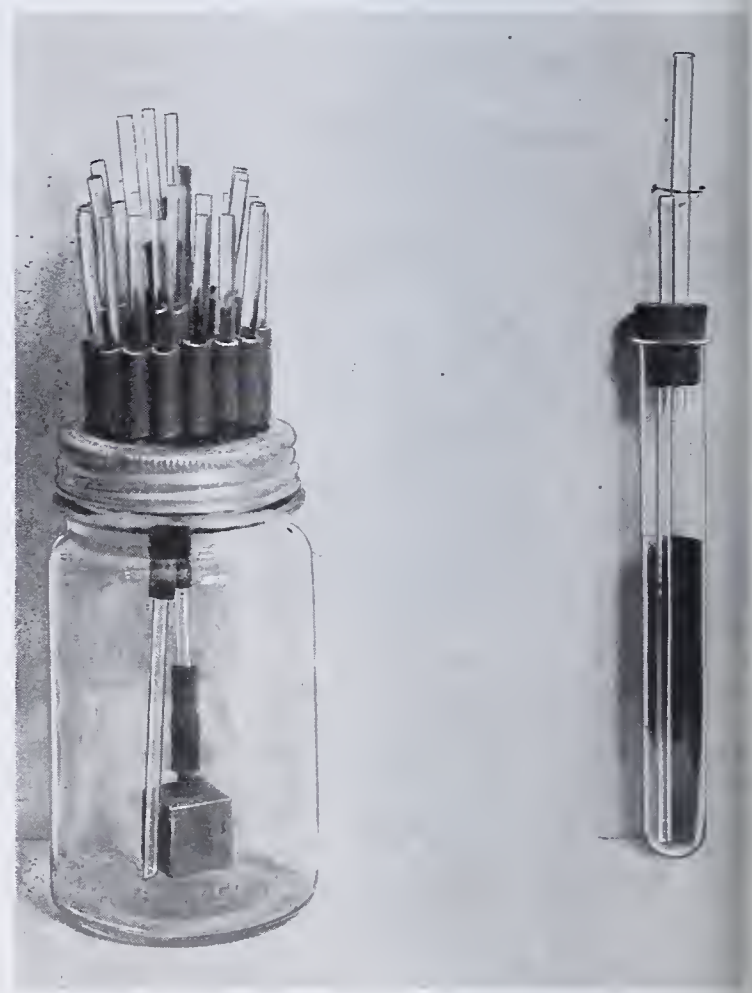


FIGURE 2. CLOSE-UP OF AIR DISTRIBUTOR AND OF TEST-TUBE ASSEMBLY USED IN PRELIMINARY CORROSION TESTS

At the end of the test, the metal strips are removed as quickly as possible and wiped dry. They are then washed with soap and water, followed by the toluene-ethyl acetate rinsing as described above. The strips are kept in a desiccator at all times while awaiting use or weighing. The extent of corrosion is expressed in terms of loss in weight, since all specimens have approximately the same surface area. The type of corrosion—e. g., pitting—is also always noted and recorded. Observations of the appearance of the solution and the metals are made periodically



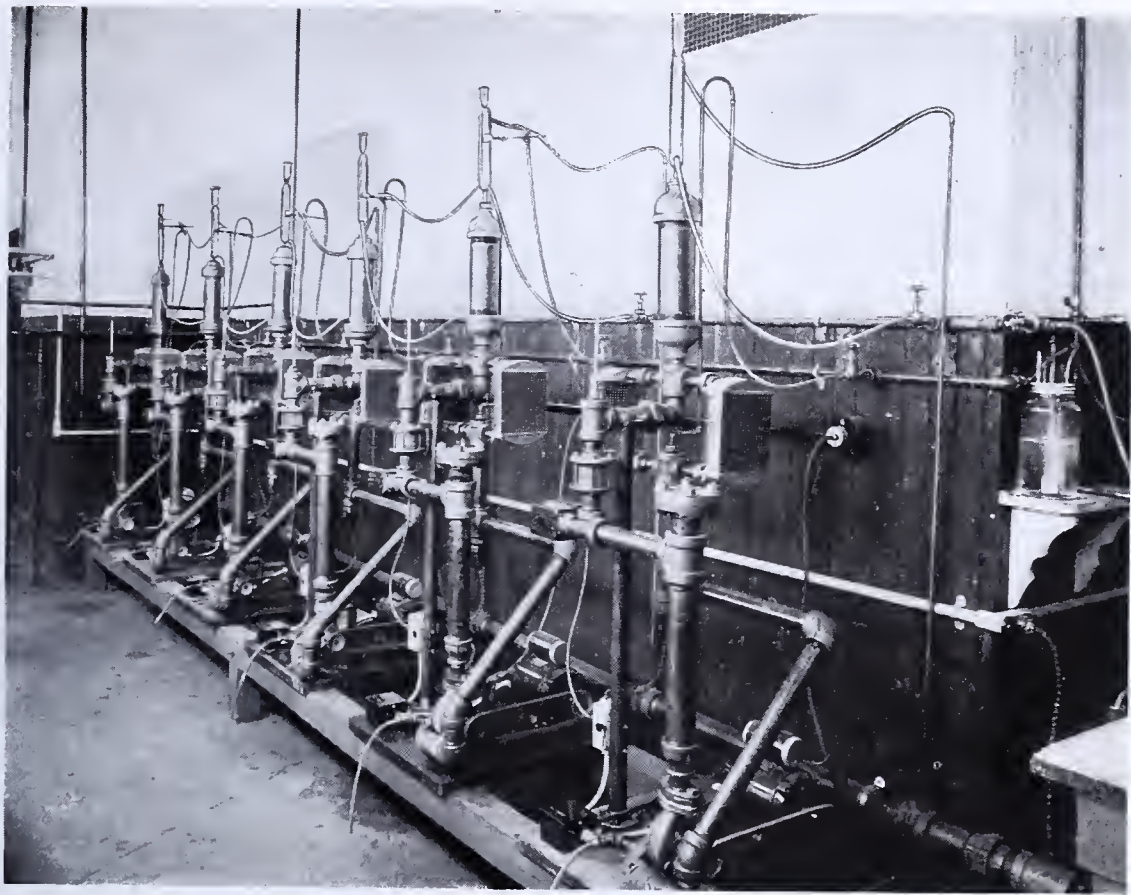


FIGURE 3. BATTERY OF CIRCULATING UNITS USED IN FINAL LABORATORY EVALUATION OF CORROSIVE PROPERTIES OF ANTIFREEZES

during the test and at the end of the test. The pH of the solution is also determined before and after the test.

Breakdown of an antifreeze solution is considered as the point where rusting begins. This is more or less arbitrary, since severe corrosion of some other metal may occur before rusting begins. Hence, these tubes are removed at the first appearance of rust and the strips are cleaned and weighed. If no rusting has occurred at the end of 6 weeks, the tests are stopped because it has been found that any solution, which will undergo the conditions imposed for 6 weeks without serious attack on steel, brass, and solder, is worthy of a larger scale test.

Preliminary tests such as the above, however, are not considered severe enough for final laboratory evaluation, nor do they approach the actual conditions of usage to which an antifreeze solution is subjected. It is necessary, therefore, to test an antifreeze under conditions as nearly duplicating those found in an automobile cooling system as is possible in the laboratory. For this purpose, the authors use the equipment shown in Figure 3. These testing units were designed to simulate the essential conditions of automotive usage, yet permit control of conditions within narrow limits, so that these can be duplicated in succeeding tests.

In these larger scale tests, the antifreeze solution is circulated continuously through a system having an operating capacity of about 6.43 liters (1.7 gallons) and made up for the most part of 25-inch iron pipe to represent the large amount of iron surface found in the automotive engine jacket. Special care was used in choosing the size of the pipe and all of the equipment through which the solution circulates so as to have no restricted flow. This is important because with restricted flow there would be a high-pressure differential between the intake and output sides of the pump, which would aggravate leakage. Circulation is accomplished by means of a regular automobile water pump,<sup>1</sup> belt-driven by an electric motor at a speed of

2200 r. p. m., which is roughly equivalent to an automobile speed of 30 miles per hour. Incorporated in the system are two copper radiator cores of the type used in automobile hot-water heaters. These represent the radiator of a cooling system. The solution is heated by an iron-jacketed electric immersion heater. The iron-jacketed type was chosen because in an automobile engine heat is transmitted through the iron of the cylinder walls to the cooling liquid; so also here the heat is transmitted from its source through iron to the solution. The temperature is automatically regulated by a Penn type LL thermostat which maintains the temperature within 2° C. of that desired. A length of regular automobile rubber radiator hose connects the intake of the pump with the remainder of the system. A sight glass is inserted in a convenient place so that the appearance of the solution can be observed. A loose 25-cm. (10-inch) length of 1-inch pipe, dropped in a vertical position into the top chamber, precludes the possibility of any static condition prevailing in this reservoir.

Throughout a test, the solution being circulated is aerated at a constant rate (25 cc. per minute), providing oxygen so that corrosion can proceed at a maximum rate. This amount of air was shown by experiment to contain oxygen in excess of that used during the most severe conditions of corrosion. The pump provides enough suction to take in this air, and the rate is controlled by insertion of a capillary of the necessary bore and length in a piece of rubber tubing connected to a small opening in the system on the suction side of the pump. As mentioned previously, in testing volatile-type antifreeze solutions, provisions must be made to prevent evaporation losses caused by aeration. The capillary, therefore, is connected with a source of air which is kept saturated with vapors of a solution of the same concentration as that being used in the test. A water condenser is used on the outlet of the top reservoir to condense vapors carried out by the air passing through the solution. In cutting the threads on the pipe used in constructing the units, some of the cutting oil usually gets down on the inside of the pipe. To prevent this cutting oil from affecting the corrosion results, each section of pipe is thoroughly cleaned internally with a mixture of equal volumes of toluene and ethyl acetate. Compound used on the threads to make a tight joint is placed only on the male end of the joint, so that it does not come in contact with the solution being tested.

After the completion of a test, the unit is dismantled and all of the iron pipe, joints, radiator, water pump, and hose connection are discarded and replaced by new parts when the unit is rebuilt. The few small brass parts used, the electric heater, and thermo-

<sup>1</sup> Nash Lafayette "400" (assembly No. 3728). This pump was chosen because it is one of the few independently mounted pumps now available.



stat are thoroughly cleaned, so as to avoid any contamination from the previous test.

Test disks of five different metals—soft steel, copper, brass, aluminum, and solder—of the following dimensions are ordinarily used in these tests: thickness, No. 16 B. & S. gage; diameter, 3.82 cm. (1.5 inches). These disks have a 0.64-cm. (0.25-inch) hole in the center to fit on a 0.64-cm. (0.25-inch) brass rod which is screwed in the brass cap of the test-piece chamber. This chamber is the 2-inch pipe extending upward from the discharge side of the pump, and is of sufficient length to accommodate eight sets of disks which are kept apart by 0.64-cm. (0.25-inch) brass spacers made from 0.125-inch brass pipe (Figure 4).

Before starting a test, the pump is repacked with a good grade of graphited asbestos packing. It is usually not necessary to repack the pump during a test. The unit is then filled with water, which is circulated at operating temperature for 24 hours. This 24-hour period is called the "prerust" period and serves several purposes, chief of which is to form a coating of rust on all the iron surfaces of the system. This is the condition found in the average automobile cooling system when an antifreeze is added. Less important functions of the prerust period are the opportunities it presents to check the unit for leaks and to regulate the thermostat to the temperature desired without interfering with the test. Two sets of test disks are placed in the test chamber during the prerust period. One set is removed and weighed after the prerust period, while the other set remains in the system along with the other seven sets which are put in. By comparing the losses in weight of these two sets of disks and the last set taken from the test during a run, a check can be made as to whether the antifreeze solution preferentially attacked freshly prepared and cleaned metal surfaces over previously corroded surfaces.

When the 24-hour prerust period is ended, the unit is drained and thoroughly flushed with water so as to remove all loose rust. Seven sets of weighed test disks are placed in the test chamber, 6300 cc. of the antifreeze solution of a concentration which freezes at  $-20^{\circ}$  F. are added, and the unit is started. The air flow through the system is checked once each day with a eudiometer and is kept at  $25 \pm 2.5$  cc. per minute. The pH of the solution is determined once each week, and even more often near the time that rusting begins. This is especially important in the testing of antifreeze solutions of the polyhydric alcohol type where the inception of rusting, of breakdown of the solution, may be accompanied by a marked drop in pH. The speed of the pump is also checked once each week and is maintained at  $2200 \pm 50$  r. p. m. by adjustment of the driving belt.

One set of test disks is removed and weighed each week under ordinary circumstances. However, in cases where the antifreeze solution being tested is expected to have a life longer than 7 weeks, the first two or three sets may be removed at longer intervals, say, 2 weeks. As soon as rusting is indicated, a set of disks is removed and weighed. Any remaining sets are removed at 1- to 2-day intervals. Observations are made daily of the appearance of the solution as seen through the sight glass; it is not difficult to note the first appearance of rust. Test pieces are cleaned and handled in the same manner for these tests as described previously for the preliminary tests.

### Storage Tests

Most present-day antifreezes are packaged in sealed cans, and this fact adds another to the long list of tests which an antifreeze must pass before it is pronounced satisfactory. Sometimes as much as a year or two elapses between the times of packaging and use. Therefore, an antifreeze must have good storage qualities. It must not corrode the package, and it must not lose its corrosion-inhibiting qualities on storage.

The authors make these tests in 0.473-liter (1-pint) friction-top cans. The cans are filled with the antifreezes under test and stored away at room temperature; every 3 months the cans are opened and observations are made as to any corrosion of the can which has taken place, or any change in appearance of the antifreeze, such as the appearance of a solid, or

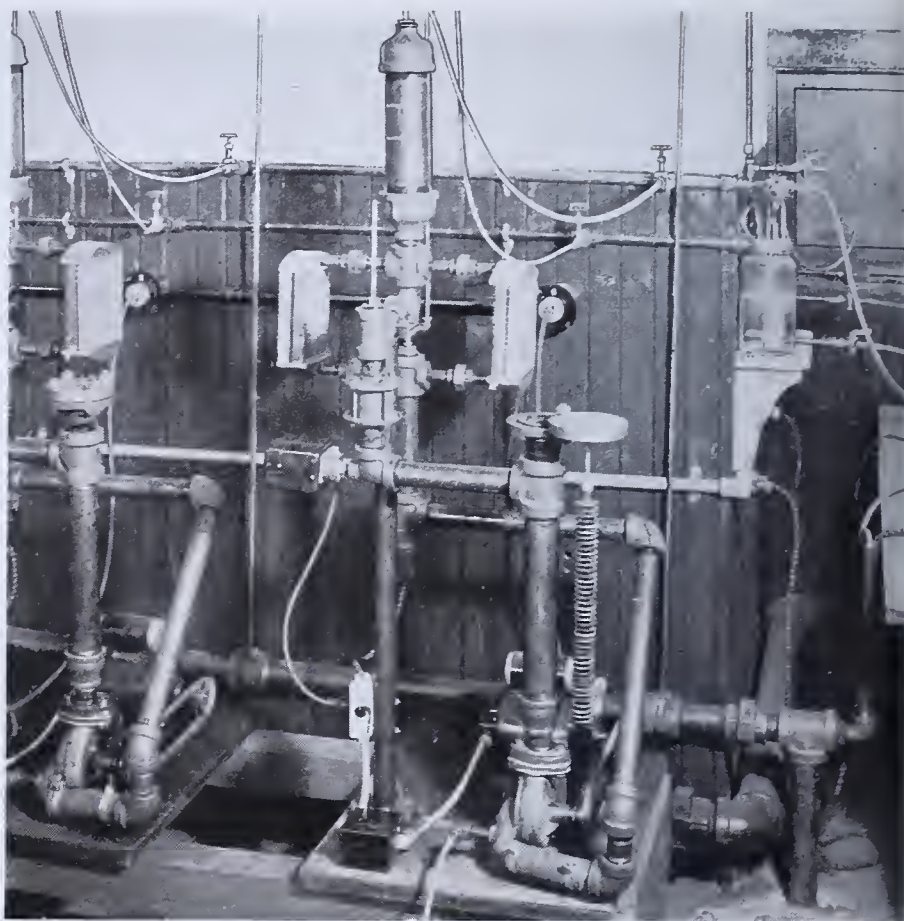


FIGURE 4. CIRCULATING UNIT, SHOWING TEST DISK ASSEMBLY REMOVED

another liquid phase. At the end of a year, a small-scale corrosion test of the antifreeze is made to determine whether it has retained its original corrosion-inhibiting properties.

### Attack of Rubber

Attack of rubber by antifreeze solutions is important, because in an automobile cooling system the solution is constantly in contact with a large area of rubber surface in the form of rubber hose connections. While it is true that the basic material present in the antifreeze determines to a great extent the action of the antifreeze solution on rubber, materials added to the basic component to improve other qualities may also affect its behavior towards rubber. For this reason an antifreeze should be tested for possible attack on rubber by either of the two satisfactory methods described below.

In one method, a section of actual radiator hose is immersed in the antifreeze solution which is maintained at the normal operating range of temperature for 6 weeks. The section of hose is then removed, and the extent of swelling measured and the appearance noted.

In the other method which the authors use, an examination is merely made at the end of the test of the hose connection used on the large-scale corrosion testing units previously described. If the hose connection survives a 5- to 6-week test on this unit without undue swelling or loss in mechanical strength, the antifreeze is considered satisfactory in this respect. This test is preferable because it closely approximates actual conditions of usage.

### Foaming

Foaming of an antifreeze solution is highly undesirable for obvious reasons, the most important being the loss of solution from the cooling system via the overflow pipe. The chief aids to foaming are aeration and agitation, both of which ex-



ist in the corrosion tests in the circulation units previously described. Any tendency to foaming should, therefore, manifest itself during these tests. Observations are made periodically for evidence of foaming. A solution which foams to any serious extent will foam up into and out of the top of the reflux condenser which is located on the top reservoir of the unit.

### Field Tests

Notwithstanding the care which is taken in making laboratory tests, and the effort which is made to duplicate actual conditions of use in an automobile, it is difficult to simulate all conditions. This could probably be accomplished if all automobile cooling systems were constructed exactly alike. Unfortunately, however, they all differ in some way, so that if the investigator simulates one particular cooling system in his laboratory tests, then his conditions of test and construction of equipment will not be wholly applicable to another.

Cooling systems of various makes of automobiles are likely to differ in one or more of the following characteristics: constructional design, materials of construction, metallic couples, rate of circulation, amount of aeration, and operating temperature.

It becomes necessary, therefore, in making the final evaluation of a new antifreeze, to employ field tests in a wide variety of automobiles under various conditions of use. Accurate comparative results cannot be obtained by road tests, it is true, because conditions cannot be controlled, but these tests do occasionally reveal a fault in an antifreeze which did not manifest itself in laboratory tests.

### Acknowledgment

Earlier forms of the corrosion-testing equipment described herewith were originally developed by the senior author at The Miner Laboratories in connection with research fellowships of the Association of American Soap and Glycerine Producers, Inc.

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# Viscosity Measurement

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Viscosity and viscosity temperature coefficients are valuable identifying properties of pure compounds and petroleum fractions. This paper discusses the operating characteristics of simple modified Ostwald viscometers that are suitable for covering a wide range of viscosity with accuracy. The important sources of error in capillary viscometers are analyzed briefly and equations for computing the necessary corrections are given. Comparisons are made with other types of capillary viscometers which show that the modified Ostwald is equal in accuracy to any now available.

FOR many years viscosity and viscosity-temperature coefficients of petroleum fractions have been regarded as important physical constants. The work of Mikeska (8) and Viggins (13) on organic compounds shows these properties to be valuable identifying characteristics that will doubtless find greater application in future work. Since viscosity is intimately associated with structure, constitution, symmetry, clarity, saturation, and molecular size, it may be employed as a means of analysis. For example, the data of Viggins (13) show the viscosity of diallyl, the diolefinic derivative of hexene, to be 15 per cent less than hexane at 0° C. and toluene differs from methylcyclohexane in viscosity by more than 20 per cent at 0° C. Many high-boiling petroleum fractions of

identical boiling points differ in viscosity by several hundred per cent.

It is the purpose of this paper to describe briefly suitable capillary-type viscometers for measuring viscosity in a simple but precise manner. In addition, the sources of error and their magnitude will be discussed, together with means of rendering these negligible.

Figure 1 is an illustration of an accurate routine viscometer, particularly designed for petroleum fractions, which is now in extensive use in the petroleum industry both in this country and abroad. A complete description and operating technic have been recently published by the American Society for Testing Materials (1).

The extra bulb on the capillary side of the instrument is for the purpose of incorporating an accurate loading device as an integral part of the viscometer. A glass bridge joins the two legs of the viscometer as shown; in addition heavy-walled glass is used throughout, so that the instrument is not fragile. Practically any size of working capillary can be used in the viscometer, so that very viscous fluids such as heavy lubricating oils can be tested quickly and accurately. For example, a series of four such instruments of different capillary bores will conveniently cover a viscosity range of 2 to 1000 centistokes: The instrument of smallest bore would be for a range of 2 to 10 centistokes, the next for 6 to 40 centistokes, the next for 30 to 200 centistokes, and the fourth for 150 to 1000 centistokes. Because of the low cost and ease of construction, it is possible to obtain viscometers with bores most convenient for the particular viscosity range in question. Six cubic centimeters of liquid are required for a test. The overall length of the instrument is approximately 25 cm. Six or more will readily fit into a small constant-temperature bath.

### Operation of Modified Ostwald Viscometer

The viscometer is loaded at room temperature by holding it in an inverted vertical position with the capillary side submerged



in the liquid under test. Suction is then applied to the other arm of the instrument and both small bulbs on the capillary arm are filled with oil. The liquid is brought into the working capillary to the etched mark; hence, the total charging volume is that held by the two bulbs plus that held by the capillary extending to the open end of the instrument. After filling, the viscometer is revolved to its normal vertical position and placed in the constant-temperature bath. The liquid will drain into the lower reservoir during the time required for it to attain the bath temperature. When this temperature is reached, the efflux time is obtained by drawing the liquid up to the mark between the bulbs and measuring the time required for the meniscus to pass from the mark between the bulbs to the mark below the lower bulb on the capillary. The viscosity of the fluid is then obtained by multiplying the efflux time in seconds by the viscometer constant. The evaluation of the viscometer constant is discussed later. The only function of the upper bulb on the capillary arm is to serve as an accurate loading device in conjunction with the end capillary and efflux bulb. Laboratory experiments show that the instrument and liquid contents will reach a bath temperature of 37.78° C. (100° F.) in about 4 minutes and a temperature of 98.8° C. (210° F.) in approximately 10 minutes.

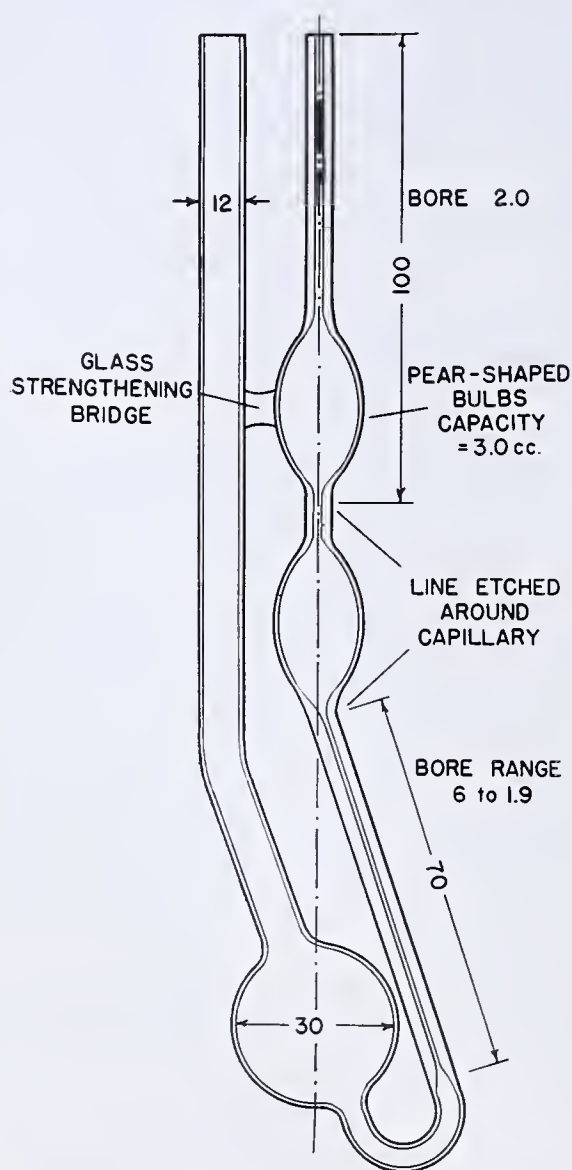


FIGURE 1. ROUTINE VISCOMETER FOR PETROLEUM PRODUCTS  
Dimensions in mm.

A viscometer more suitable for nonviscous liquids is illustrated by Figure 2. This instrument differs from Figure 1 in several respects. The efflux volume and working capillary are considerably smaller and the diameters of the efflux bulb and the lower reservoir (actually part of the larger arm) are the same. These changes were made to reduce kinetic energy and surface tension corrections, but are not incorporated in the

routine type (Figure 1), first, because no kinetic energy corrections are encountered in products of 2 centistokes or more in these instruments if properly used, and secondly, because petroleum fractions do not differ sufficiently in surface tension to become an appreciable source of error. It will be shown later that a large difference in surface tension will necessitate only a small correction.

This second viscometer has an over-all length of approximately 30 cm. and requires a 2.5-cc. charge. The efflux bulb has a volume of 1.0 cc. It is recommended for viscosities ranging from 0.3 to 5 centistokes. It can be used for more viscous liquids, but the type shown as Figure 1 is more convenient for the higher viscosity range.

A semimicroviscometer (Figure 3) has an over-all length of approximately 30 cm. and requires a total charge of 0.25 cc. It can be made with practically any desired capillary bore to cover a range of 0.5 to 800 centistokes. The efflux volume is approximately 0.15 cc. and the efflux capillary and lower reservoir capillary are of the same diameter to eliminate surface tension corrections. Although the over-all length of these instruments is 30 cm., the length submerged in the bath is approximately 20 cm., so that a constant-temperature bath that is 20 cm. deep is suitable.

### Magnitude and Source of Errors

Loading errors arise from the fact that the driving fluid head is dependent upon the amount of liquid in the instrument. Thus, if too much liquid is charged to the instrument, the level in the lower reservoir is too high and driving head is reduced by that amount. The expression for loading errors is:

$$\% \text{ error in loading} = \frac{100 \nu}{\pi r^2 H}$$

where  $\nu$  is the loading error,  $r$  is the working radius of the lower reservoir, and  $H$  is the driving liquid head.

As a specific example of the magnitude of this error, consider a routine type of viscometer (Figure 1). In these instruments  $H$  is approximately 10 cm.,  $r$  is 1.5 cm., and a working capillary of 0.1-cm. diameter will be considered. If, when loading, the operator misses the etched mark on the capillary by 0.1 cm., then  $\nu$  will be 0.00079 cc. and the percentage error 0.001 per cent. To make an error of 0.1 per cent it would be necessary for the operator to miss the etched mark on the capillary by 12 cm. The viscometers shown as Figures 2 and 3 are more sensitive to loading errors, but the error is readily maintained below 0.1 per cent. The validity of this loading error equation was proved by weighing into several viscometers a known excess of test liquid and checking the results obtained with those predicted by the equation. Checks were also made by withdrawing known amounts, so that a deficient quantity of liquid was in the instrument. In all cases the experimental results agreed with those predicted by the equation.

Kinetic energy corrections are primarily due to contraction and expansion losses at the entrance and exit of the capillary. It is customary (2) to include the kinetic energy correction in Poiseuille's equation as follows:

$$KV = \frac{\omega}{\rho} = \frac{\pi g H r^4 t}{8 L V} - \frac{m V}{8 \pi L t}$$

where  $KV$  = kinematic viscosity in stokes

$\omega$  = viscosity in poises

$\rho$  = density in grams per cc.

$g$  = gravitational constant in cm. per sec. per sec.

$H$  = fluid head in cm.

$r$  = radius of capillary in cm.

$t$  = efflux time in seconds

$L$  = capillary length in cm.

$V$  = efflux volume in cc.

$m$  = kinetic energy coefficient



The second term on the right side of this equation is the kinetic energy correction. In a properly designed instrument this term should be very small compared with the first term on the same side of the equation. The percentage error or correction is more important than the absolute figure. The expression for the percentage correction can be obtained by dividing the kinetic energy term by the main term and multiplying by 100.

Kinetic energy correction in per cent =  $\frac{mU^2}{gH} 100$

The velocity in the capillary is given by  $U$ . From this expression it is obvious that kinetic energy corrections will increase as the square of the velocity in the capillary.

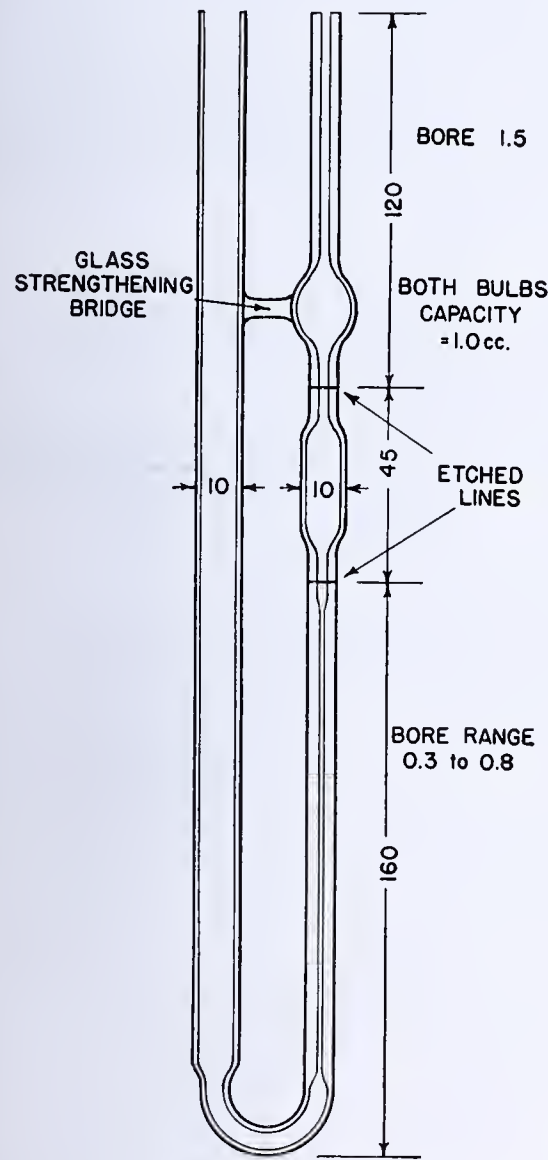


FIGURE 2. VISCOMETER FOR NONVISCIOUS FLUIDS  
Dimensions in mm.

For most types of viscometers the correct value of  $m$  is not known, but it is probably intimately associated with the shape of the entrance and exit of the capillary. Values of  $m = 0$  to  $m = 1.12$  have been reported (2). In all the instruments discussed here the capillary openings are gradually tapered to give a trumpet-shaped opening. Bingham and Thompson (3) report a value of  $m = 0.56$  for such openings. Granted that this value may not apply to other capillaries of similar construction, nevertheless it is probably of the proper magnitude and may be used to calculate the permissible velocity range in a

capillary so that kinetic energy corrections may be maintained below 0.2 per cent. This was verified by testing water at two different temperatures in each of two viscometers with capillaries of different size.

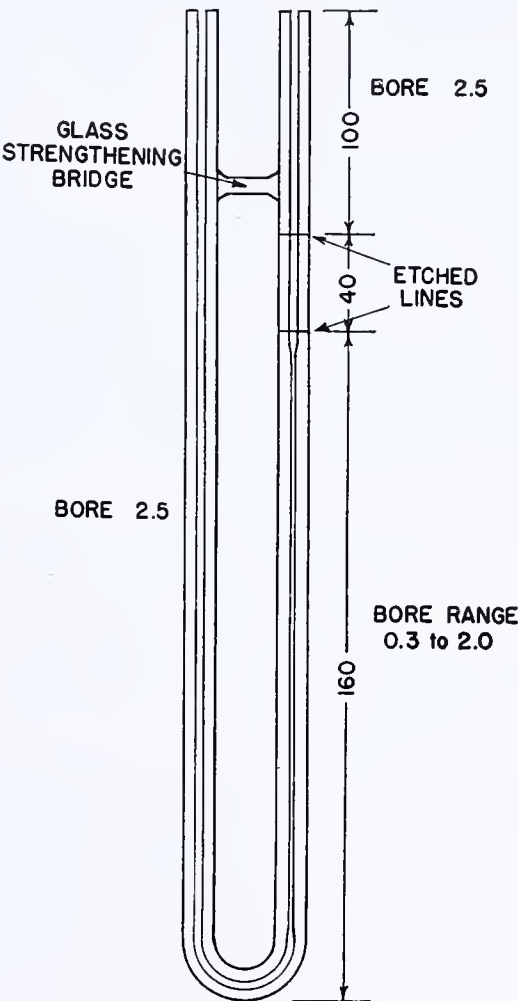


FIGURE 3. MICROVISCOMETER  
Dimensions in mm.

The kinetic energy term needs special attention only when designing instruments for nonviscous liquids (2 centistokes or less). In viscometers designed for more viscous liquids the capillary is large enough to make this correction negligible. Since the value of  $m$  is not accurately known, it is not safe to allow the kinetic energy correction to become appreciable and attempt to apply this correction to the results. There is no assurance that  $m$  is a constant for a given instrument; it may vary with the velocity of the liquid in the capillary in addition to the shape of the capillary openings. It is a simple matter to construct a viscometer with dimensions such that the calculated kinetic energy correction is less than 0.2 per cent for liquids as low as 0.5 centistoke in viscosity. The viscometer shown as Figure 2 differs in its dimensions from that shown as Figure 1, mainly for the purpose of eliminating kinetic energy corrections. These corrections are not encountered in the first viscometer, since it is designed to cover a range of viscosity from 2 centistokes upward. The microviscometers are free from kinetic energy corrections if the dimensions are properly selected. It is obvious that the efflux volume and capillary diameter should be made small in order to reduce the kinetic energy correction. It is also reduced by increasing the driving fluid head—i. e., the distance between the efflux bulb and the lower reservoir.

As the fluid stream emerges from the capillary, it has a tendency to retain the shape of the capillary for a finite distance into the fluid medium. This apparent increase in capillary



length, known as the Couette correction, is a function of the capillary radius. It is included in the viscometer constant established by calibration.

Drainage errors arise from the fact that all liquids do not drain from a surface with equal ease; hence, the measured efflux volume for one fluid may be different than for another. In a series of experiments performed to measure drainage errors (4) it was shown that these are of negligible magnitude. In addition to the possible effect on efflux volume, Fitzsimons (6) pointed out that drainage will affect the liquid head. The experimental drainage measurements indicate that this effect will never change the liquid head by 0.01 per cent in viscometers of the type described here.

If there is a considerable difference between the surface tension of the calibrating fluids and the fluids subsequently tested, an error due to capillarity will arise. Although the familiar capillary-rise equation will not hold rigidly for tubes of large diameter, it may be employed to determine the magnitude of this error. It can be readily shown that the change in effective driving head due to surface tension difference is approximated by the following equation:

$$\Delta H = \left(\frac{2}{g}\right) \left[\frac{1}{r_1} - \frac{1}{r_2}\right] \left[\frac{ST_1}{d_1} - \frac{ST_2}{d_2}\right]$$

where  $\Delta H$  = change in effective driving head  
 $r_1$  = working radius of efflux bulb  
 $r_2$  = working radius of lower reservoir  
 $ST_1$  = surface tension of calibrating fluid  
 $ST_2$  = surface tension of test fluid  
 $d_1$  = density of calibrating fluid  
 $d_2$  = density of test fluid

Hence, if an instrument of the type presented as Figure 1 were calibrated with water at a temperature where the surface tension is 70 dynes per centimeter and then used on oils whose surface tension is 30 dynes per centimeter, the change in effective head would be approximately 0.7 mm. Since the driving head is 10 cm., the percentage error introduced by neglecting the surface tension correction is 0.7 per cent. However, it is a simple matter to make this correction accurately or to calibrate the instruments by means of viscosity standards which have been standardized in master instruments especially constructed to maintain all errors negligible (5). It is evident that surface tension changes produce a very small effect, for in the case considered a change of over 200 per cent in surface tension necessitated a correction of only 0.7 per cent. The viscometers presented as Figures 2 and 3 are free from surface tension corrections because in the latter instrument the efflux and lower reservoir tubing are of the same diameter and in the instrument shown in Figure 2 practically all the efflux time is measured when the menisci of both the upper and lower levels are in tubes of equal diameter.

It is necessary to align the viscometer in the bath in an exact vertical position, so that the full available driving fluid head is utilized. If the center of the efflux bulb is joined to the center of the lower reservoir by an imaginary line which makes an angle of  $A$  degrees with the vertical, and if this should be moved  $dA$  degrees, then the resultant fractional change in the fluid head will be given by the expression:

$$1 - \frac{\cos(A + dA)}{\cos A}$$

For this to be a minimum, angle  $A$  should be zero. In other words, the upper efflux bulb and the lower reservoir should lie in the same vertical planes. With this type of construction the viscometer must be tilted  $2.5^\circ$  from the vertical to introduce an error of 0.1 per cent. A deviation of  $2^\circ$  is readily detected by visual inspection, but for safety the viscometer may be aligned vertically with the aid of a small plumb bob made from silk thread and a small piece of lead,

which is placed in the open arm of the viscometer. An experienced operator can load and align the viscometer in the bath in less than one minute. The viscometer of Figure 1 has the efflux bulb and lower reservoir directly in line for eliminating alignment errors. This modification has not been incorporated in the other two viscometers, because they are longer and readily adjusted to the vertical position. The vertical alignment of bulbs was originated by Gruneisen (2).

The viscometer constant will vary with the temperature, but the magnitude of the change is small and readily computed. This correction arises because of the change of specific volume with temperature. Thus, if the viscometer is loaded at  $25^\circ\text{C.}$  and then used at some higher temperature, say  $100^\circ\text{C.}$ , a correction should be applied. The thermal coefficients of cubical expansion of most hydrocarbons do not differ sufficiently to necessitate an individual correction for each type of compound. It is therefore possible to give simply the viscometer constant at two different temperatures, and for other temperatures one can interpolate or extrapolate. Mathematically the viscometer constant at a second temperature may be readily computed from the known constant at some other temperature by the following equation:

$$C_{T_2} = C_{T_1} \left[1 - \frac{V_2 - V_1}{0.785 H d^2}\right]$$

where  $C_{T_2}$  = viscometer constant at temperature  $T_2$   
 $C_{T_1}$  = viscometer constant at temperature  $T_1$   
 $V_2$  = total volume of liquid in viscometer at temperature  $T_2$   
 $V_1$  = total volume of liquid in viscometer at temperature  $T_1$   
 $H$  = driving liquid head, approximately equal to distance between centers of efflux bulb and lower reservoir  
 $d$  = working diameter of lower reservoir

This correction may be eliminated entirely by preheating the sample and the instrument to test temperature before loading. However, it is of such small magnitude and determined so readily that it is advisable simply to load the instrument at room temperature. Calibrated viscometers have the constant specified at two temperatures, so that the user may readily interpolate or extrapolate. The above correction amounts to only 0.5 per cent for a  $60^\circ\text{C.}$  change in temperature for lubricating oils and gasoline fractions in the viscometers of Figure 1. It is obvious that this correction, due to temperature, is very similar to loading errors discussed earlier. The error caused by expansion of Pyrex glass over the temperature range  $0^\circ$  to  $200^\circ\text{C.}$  has a negligible effect on the viscometer constant. Consequently, if the glass should show a hysteresis effect no appreciable error will be introduced.

A variation in the gravitational constant from the place of calibration to the place of usage will necessitate a simple correction which is made by multiplying the constant of the viscometer by the ratio of  $g$  at the point in question to  $g$  at the point of calibration. As the value of  $g$  does not change by more than 0.1 per cent throughout the United States, this correction is of secondary importance.

Dark fluids will readily absorb radiant heat energy from solar or unshielded light sources. Consequently a dark fluid under test may be several tenths of a degree higher in temperature than the bath medium in which it is immersed. Since a slight change in temperature causes an appreciable change in viscosity of most fluids, it is important that lights employed in the immediate vicinity of the bath be shielded. Table I contains data which show the magnitude of this radiant energy effect. In most practical cases lights employed for good visibility in constant-temperature baths are not more than 25 watts and are placed in the rear, so that their distance from



the working area of the bath is greater than 10 cm. (4 inches). In most installations their effect will be small, but if proper care is not exercised the error so introduced may be of consequence.

TABLE I. MAGNITUDE OF TEMPERATURE INCREASE IN LIQUIDS CAUSED BY RADIANT ENERGY FROM UNSHIELDED LIGHT BULBS

Liquid	Color	Type of 110-Volt Light Bulb	Distance of Bulb Surface from Bath Surface	Temp. of Liquid	Temp. of Water Bath	Difference
			Cm.	° C.	° C.	° C.
Lube oil	A. S. T. M. No. 7	100-watt frosted	1.25	38.41	37.78	0.63
			5.00	38.19	37.78	0.41
			10.00	38.07	37.78	0.29
		75-watt frosted	1.25	38.06	37.78	0.28
			5.00	37.92	37.78	0.14
			10.00	37.89	37.78	0.11
		50-watt frosted	1.25	37.86	37.78	0.08
			5.00	37.84	37.78	0.06
			10.00	37.81	37.78	0.03
Lube oil	A. S. T. M. No. 2.5	100-watt frosted	1.25	38.36	37.78	0.58
			5.00	38.13	37.78	0.35
			10.00	38.02	37.78	0.24
		75-watt frosted	1.25	38.04	37.78	0.26
			5.00	37.94	37.78	0.16
			10.00	37.89	37.78	0.11
		50-watt frosted	1.25	37.86	37.78	0.08
			5.00	37.84	37.78	0.06
			10.00	37.82	37.78	0.04
Water	.....	100-watt frosted	1.25	37.83	37.78	0.05
			5.00	37.80	37.78	0.02
			10.00	37.79	37.78	0.01
		75-watt frosted	1.25	37.80	37.78	0.02
			5.00	37.79	37.78	0.01
			10.00	37.78	37.78	0.00

The constant-temperature bath was of 36-liter capacity and was filled with water. The walls were of Pyrex glass approximately 0.6 cm. thick. The Pyrex test tube containing the sample was 5 cm. from the inner bath surface.

The data of Table I were obtained at 37.78° C. (100° F.) because it is a standard test temperature in the petroleum industry. The measurements were made by placing the fluid under test in a Pyrex test tube and then immersing it in a constant-temperature water bath automatically controlled at 100° F. to within ±0.05° F. Temperature measurements were made by very sensitive Bureau of Standards calibrated thermometers. In the experiments where water was tested, the radiant heat was probably picked up by the thermometer bulb rather than by the water. The magnitude of the actual errors in viscosity caused in this way depend upon the viscosity temperature coefficient of the fluid at the test temperature. Many heavy oils change in viscosity by 0.2 per cent with a temperature change of 0.1° F. in the vicinity of 100° F. At lower temperature levels the effect would be more pronounced because viscosity temperature coefficient increases with decreasing temperature level.

Calibration of Viscometers

A nearly ideal reference basis for viscosity work is pure water. Instruments which are designed to cover a viscosity range in the neighborhood of water can be calibrated directly against water. When an instrument is designed to cover a range far removed from water, such as that found in lubricating oils, direct calibration is not possible. However, water may be retained as the reference basis by standardizing a series of oils in suitable master instruments and then employing these oils as calibration standards. This procedure has been explained in detail elsewhere (5). As many oils are unstable and increase in viscosity with age as much as 2.0 per cent per year, it is advisable to check the viscosity of standardized oils from time to time. Solvent-treated or aluminum chloride-desludged oils of high viscosity index are the most stable and some vary only 0.2 per cent per year.

For accurate results it is necessary to employ sensitive and reliable auxiliary equipment. Descriptions of satisfactory units have been published (5).

Comparison with Other Viscometers

Various other modifications of the Ostwald instrument are advocated by some investigators. Ubbelohde's (12) suspended-level type of instrument differs from the type described here only in eliminating loading errors and reducing surface tension errors. In the design presented here such errors are of negligible magnitude; hence either type of instrument will yield results of equal accuracy. Zeitfuchs (14) has recently described another modification of the Ostwald instrument which also reduces loading errors and undoubtedly will yield accurate results. Slight modifications of the Ubbelohde type have been described by Fitzsimons (6) and by Payne and Miller (9).

The semimicroviscometer described here is simpler than the falling-sphere type described by Schneider and McConnell (11) and is more convenient than the type described by Levin (7) where surface tension is employed as the driving force.

The viscometer recently described by Raaschou (10) is also a modification of the Ostwald tube and again the main purpose is to reduce loading errors. This is accomplished by adjusting the liquid level by visual inspection of the meniscus in a tube of large diameter (17.5 mm.). It is difficult to make such an adjustment to better than 0.5 mm. An error of this magnitude would change the driving fluid head by the same amount and introduce a percentage error of 0.5 per cent (since the total head is approximately 100 mm.). For most practical purposes such an error is of little consequence. Raaschou uses a value of 1.0074 centistokes as the viscosity of water at 20° C., whereas a value of 1.0068 centistokes has been recommended by the American Society for Testing Materials as the standard for viscosity work. While this difference is slight, it has been included in this report to cover completely the many factors involved.

It appears, then, that there are available a number of capillary-type viscometers which will yield accurate results. The prospective user can be guided in his choice by such factors as cost, simplicity of design and operation, etc.

The reproducibility of results with the modified Ostwald viscometers described in this paper is ±0.2 per cent. The accuracy of the results depends upon the accuracy with which the absolute viscosity of water is known at 20° C., since water is used as the ultimate reference basis. This error is probably in the neighborhood of ±0.5 per cent. However, relative viscosities are very accurate and if the reference basis is clearly defined little confusion will exist and reported values of viscosities may be readily compared.

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# Determination of Iron in Biological Material

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NUTRITION work being carried out in this laboratory required a method for the determination of total iron in a wide variety of biological materials, which would yield equally accurate results with all samples with only very minor modifications. Many methods for this determination have appeared in the literature, but they have all been for use on some particular material, and do not yield accurate results on other materials when only the quantities of reagents are varied. This observation led to a complete investigation of the sources of error inherent in this determination and of means by which they could be overcome. A method was developed that gave accurate results with whole rats, milk and milk products, and a large number of both fresh and dried foods.

## Determination of Iron

The determination of total iron in any organic matter resolves itself into two main steps: the ashing of the sample, and the determination of the iron in this ash. A satisfactory procedure for accomplishing the second step with any type of ash was necessary before an investigation of the merits of various methods of ashing could be undertaken. The research was accordingly planned on this basis.

The iron-containing ashes were prepared by an adaptation of Klumpp's method (6), which he used in conjunction with his titanous sulfate titration. The material was dried with a small amount of concentrated sulfuric acid (about 2 ml. per gram dry weight of the sample) and ashed in a muffle at 500° to 550° C. The ash was then taken up in hydrochloric acid, filtered, and diluted to an appropriate volume.

For various reasons a colorimetric method of determination was preferred. The titanous sulfate titration procedure of King and Howard (5) and Klumpp (6) was inconvenient, because of the special precautions needed for the preservation and use of this reagent and the large samples required, particularly of materials containing small amounts of iron. These were not always readily procurable and introduced difficulties in ashing. Moreover, the end point of the titration, while sharp with standard iron solutions, was obscured by phosphates or a high salt concentration. Colorimetric methods require much smaller amounts of iron for the determination, and the use of an Evelyn photoelectric colorimeter (1, 2) for the estimation of the color removed the personal factor inherent in all visual colorimetric comparisons.

A comparison of the relative merits of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (known as ferron, 8) and of  $\alpha, \alpha'$ -dipyridyl as chromogenic agents led to the selection of the latter. Ferron, which is itself yellow, slowly develops an additional green color in the presence of ferric iron. This color did not obey Beer's law, the pH of the solution had to be accurately controlled, and no advantages, such as immunity to interfering substances, compensated for these defects.

The use of  $\alpha, \alpha'$ -dipyridyl for the determination of inorganic iron was introduced by Hill (4) and has since been used by Elvehjem (7) for the same purpose. It was found to have somewhat more than twice the sensitivity of ferron and was not affected by pH between the limits of 2.5 and 6.0. The color developed at once on addition of the reagent to standard iron solutions (buffered to about pH 4.0 and containing hydroquinone to reduce the iron to the ferrous state). It obeyed Beer's law almost exactly and was not affected by salt concentration or by orthophosphate. However, the

presence of pyrophosphate in amounts equivalent to those that could be expected in actual analyses delayed the production of the color and prevented its full development even after standing 24 hours, at which time the color had become constant.

The first determinations were made directly on the solution of ash. The excess acidity was neutralized by the addition of 25 per cent sodium hydroxide, an accurate aliquot of this solution was buffered to a pH of about 4.0 by the addition of an acetate buffer and hydroquinone, and the  $\alpha, \alpha'$ -dipyridyl was added. The presence of pyrophosphate was at once evidenced by the slow development of the color, which reached a maximum only after 24 to 48 hours. Heating the acid ash solution prior to neutralization for 18 hours at 80° C. completely hydrolyzed the pyrophosphate to orthophosphate. With the addition of this step the color of the iron— $\alpha, \alpha'$ -dipyridyl complex developed to a maximum within a few minutes.

TABLE I. VARIATION OF TOTAL APPARENT IRON CONTENT WITH VOLUME OF ALIQUOT

Experiment	Ash Solution in Tube Ml.	Apparent Iron in Tube Mg.	Amount Expected from 1-Ml. Tube Mg.
After Hydrolysis of Pyrophosphate			
I	1	0.0020	
	5	0.0071	0.0100
II	1	0.0045	
	3	0.0108	0.0135
	5	0.0164	0.0225
III	2	0.0033	
	5	0.0060	0.0082
IV	2	0.0046	
	5	0.0085	0.0115
After Hydrolysis of Pyrophosphate and Fractionation of Iron by Ammonium Hydroxide and Hydrogen Sulfide			
V	1	0.0052	
	3	0.0153	0.0156
VI	1	0.0056	
	3	0.0170	0.0168
VII	1	0.0059	
	3	0.0172	0.0177
VIII	1	0.0099	
	3	0.0297	0.0297

By the use of this modified procedure close checks on successive aliquots of the same ash solution were obtained. However, if different aliquots were taken, the apparent iron recovered in them was not proportional to their volume. For example, if two colorimeter tubes were prepared using 1 and 3 ml., respectively, of the same ash solution (the difference in volume being made up by the addition of water), the apparent iron in the second tube was not three times the amount in the first, but somewhat less. This effect is illustrated by the first part of Table I. In every case the amount of iron found in the tubes containing the larger aliquots was considerably less than expected.

This observation led to the conclusion that an additional interfering substance or substances were present in these ash solutions. The interfering substances were not common to all materials. There was little or none to be found in cereals or in whole rats, but dried tomatoes and spinach were particularly bad offenders in this respect. Thus, while the modified procedure was satisfactory for some materials, it could not be trusted to give truthful results when applied indiscriminately to biological products in general.

It was thought that this interference might be due to some product formed during the ashing and that the difficulty might be overcome by judicious selection of a procedure for this step in the analysis. However, it was present after all



procedures that were tried, which included both wet- and dry-ashing methods. Experiments III and IV (Table I) were done on an ash solution obtained by wet-ashing dried tomatoes with nitric, sulfuric, and perchloric acids.

It was found that by precipitation with hydrogen sulfide in ammoniacal solution, following the procedure described below, the iron could be completely separated from the interfering substances, which remained in the filtrate. The iron was recovered from the precipitate by dissolving it in hydrochloric acid. The filtrate, after boiling off the excess ammonium hydroxide and hydrogen sulfide and concentrating it about four times, gave no color with  $\alpha,\alpha'$ -dipyridyl. Iron was recovered quantitatively when added to the ash solution, or when the iron standard solution alone was treated by this procedure, whether in the presence or absence of calcium phosphate. Experiments V to VIII (Table I) show that interfering substances were removed. The only difference between these two sets of experiments was the introduction of the hydrogen sulfide-ammonium hydroxide precipitation. The same sample of dried tomato was used in both cases. In each case the amount of iron found in the aliquot is closely proportional to the volume of the aliquot.

Ashing Methods

The method as thus modified could be depended on to give accurate results when applied to any type of ash. The next step in the investigation became an inquiry into the merits of the various recognized ashing procedures. The greatest difficulty to be overcome was the possibility of loss of iron as the chloride, particularly in materials containing large amounts of sodium or potassium chlorides relative to the iron content. Methods of ashing have been designed to minimize this loss as much as possible, an object which is only approximated by many.

Four methods of ashing were tried: dry-ashing with addition of sodium carbonate, dry-ashing with addition of a small amount of sulfuric acid (6), dry-ashing after covering the sample with a layer of iron-free calcium carbonate (3), and wet-ashing using nitric, sulfuric, and perchloric acids. Dry-ashing with sodium carbonate was soon discarded because of the poor checks obtained. Klumpp's and Farrar's methods gave fairly consistent checks and recoveries of added iron with an occasional erratic result. Wet-ashing gave consistently good checks and iron recoveries. As a final test of the efficiency of these three methods, an organic solution containing a known amount of iron was prepared and ashed. This solution consisted of 7.5 per cent of glucose, 2.5 per cent of urea, 100 mg. per cent of calcium phosphate, 100 mg. per cent of sodium chloride, and 1.00 mg. per cent of iron added as a standard iron solution dissolved in hydrochloric acid. When 10-ml. aliquots of this solution were dried down and ashed, with Klumpp's method the best recovery was 54 per cent of the known iron content, while most of the recoveries were about 40 per cent. The recoveries with Farrar's calcium carbonate method were 80 to 87 per cent, much better than Klumpp's, but still not good enough. When the glucose-urea solution was wet-ashed, the recoveries were 100 per cent, with an error of  $\pm 1$  per cent. Wet-ashing was thus demonstrated to be the only acceptable method of those tested. The following method of analysis was finally adopted for general application.

Method

A convenient sized sample of material, containing at least 0.02 mg. of iron, was accurately measured and placed in a 300-cc. Kjeldahl flask. If the sample was a dry powder, a few milliliters of water were added. Five milliliters of nitric acid (distilled to remove iron impurities) and 1 cc. of concentrated sulfuric acid were added, and the flask was gently heated so that

the solution was just boiling. Further 5-ml. additions of nitric acid were made as the solution began to char, until the oxidation had practically ceased. One milliliter of perchloric acid was then added and the flask was heated slightly more vigorously until white fumes began to form. Heating was stopped at this stage if the solution was colorless; otherwise, it was continued until this point was reached. After cooling, the solution was diluted to about 25 ml. Usually the solution was clear, but if a precipitate of calcium sulfate was present, as with milk samples where there is a large proportion of calcium to iron, this was filtered off and the filter paper washed.

A drop of bromophenol blue was added to the acid ash solution and concentrated ammonium hydroxide added until the acid was neutralized. About 3 ml. excess ammonium hydroxide was then run in, a total of 8 ml. usually being required, and hydrogen sulfide was passed in until the solution became saturated. It was allowed to stand a few minutes and filtered by suction on a fine Jena glass filter, the filtrate being discarded. This type of filter would pick up a precipitate so finely dispersed as to appear only as a faint green coloration, if visible at all. Care was taken not to suck the precipitate dry, as this might result in some loss of iron due to oxidation to the soluble sulfate. Without washing, the precipitate was dissolved in 1.0 ml. of 1 to 1 hydrochloric acid. The Kjeldahl flask was rinsed into the filter once with 1 ml. of 1 to 1 hydrochloric acid and several times with small amounts of water, and the whole was sucked through the filter, which was washed several times with water. The combined filtrate and washings were boiled to remove excess hydrogen sulfide, and effect solution of any colloidal sulfur. After cooling, the solution was quantitatively transferred to an appropriate volumetric flask and the excess acidity neutralized with 25 per cent sodium hydroxide. The solution was left sufficiently acid to remain perfectly clear. It was then diluted to the mark.

The Evelyn photoelectric colorimeter (1, 2) was used for the actual determination of the iron.

An accurately measured aliquot of the iron solution containing about 0.01 mg. of iron was placed in a colorimeter tube and 3 ml. of an acetate buffer containing 83 grams per liter of sodium acetate and 120 ml. per liter of glacial acetic acid were added, with sufficient water to bring the total volume to 12 ml. About 50 mg. of hydroquinone, gaged roughly on the tip of a spatula, was dissolved in the solution. On the addition of 1 ml. of 0.1 per cent  $\alpha,\alpha'$ -dipyridyl solution, the characteristic pink color developed immediately. A blank was carried through the entire procedure at the same time. The color was estimated with the colorimeter, using Evelyn's filter 520 and setting the galvanometer to read 100 with the blank in place in the tube holder. By so doing, the effect of any iron contamination in the reagents was automatically eliminated. The use of a wet-ashing procedure largely prevented the formation of pyrophosphates. However, if there was any delay in the maximum color development, the iron solution was acidified and heated, and the iron estimation repeated.

TABLE II. IRON CONTENT DETERMINED BY FINAL METHOD  
(Duplicates carried through entire procedure)

Material	Galvanometer Reading	Iron in Tube Mg.	Iron Found Mg./100 g.
Dried spinach and corn-starch	68.5	0.0079	3.95
Pabulum	69	0.0077	3.85
	71.5	0.0069	27.6
	71.25	0.0070	28.0
Dried spinach	58.5	0.0112	44.8
	59	0.0110	44.0
Cornstarch	70.75	0.0072	1.80
	70.75	0.0072	1.80
Farina	83	0.0038	0.95
	83.75	0.0036	0.90
Milk powder	67.5	0.0082	1.37
	68	0.0080	1.33
Whole rat (aliquots of same ash solution)	37	0.0210	7.0
	37	0.0210	7.0 (mg. in total rat)

The amount of iron in the volume of unknown added to the colorimeter tube for the corresponding galvanometer reading was read directly off a previously determined calibration curve.

Alternatively, the value could be calculated from the



formula  $M = \frac{2 - \log G}{K}$ , where  $M$  = mg. of iron in the aliquot added to the tube,  $G$  = corrected galvanometer reading, and  $K$  = a constant. For this determination  $K$  varied slightly from 20.6 in the range of  $M = 0.005$  mg. to 21.9 in the range  $M = 0.020$  mg. Table II shows some results on widely varying materials.

### Summary

A general method for the determination of total iron in biological materials with  $\alpha, \alpha'$ -dipyridyl is described in detail.

Evidence is given for the interference of pyrophosphate and of a second unidentified substance or substances with

the development of the color. Steps are included in the procedure which successfully circumvent these difficulties.

Various ashing procedures have been investigated.

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## Cerate Oxidimetry

### Evaluation of Solutions Using Sodium Oxalate, Arsenious Acid, and Iron as Standards of Reference, and Ferroin and Nitro-Ferroin as Indicators

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CERATE oxidimetry involves the use of the anions  $\text{Ce}(\text{ClO}_4)_6^{--}$ ,  $\text{Ce}(\text{SO}_4)_3^{--}$ ,  $\text{Ce}(\text{NO}_3)_6^{--}$ , and  $\text{Ce}(\text{ClO}_4)_6^{--}$  in the form of the free acids or their ammonium or potassium salts. The first paper of this series (2) has shown that the single-electrode potentials at standard state for these cerate anion species in equilibrium with the cerous ion in hydrochloric, sulfuric, nitric, and perchloric acid solution increase in the order given by 200, 150, and 100 millivolts, starting with the value 1.28 volts in the case of the hexachlorocerate ion and ending in the value 1.7 volts in the case of the hexaperchlorato cerate ion. With conditions defined for the attainment of potentials in the range 1.6 to 1.86 volts using cerate solutions in nitric and perchloric acid of various strengths, favorable effects in the oxidation of various reductants might be expected.

It is the purpose of the present paper to point out the increased facility with which the oxalate ion can be determined using the higher potentials provided by cerate oxidimetry. The accuracy obtained has been tested, using as additional standards of reference arsenious oxide and ferrous sulfate solutions that were standardized by comparison with the sulfato cerate ion in sulfuric acid solution through the medium of sodium oxalate. A further objective in the present paper is the description of the advantages attained by the use of nitro-ferroin (nitro-*o*-phenanthroline ferrous ion) as compared to ferroin (*o*-phenanthroline ferrous ion) as a reversible oxidation-reduction indicator in cerate oxidimetry.

The determination of the oxalate ion using the sulfato

cerate ion in sulfuric acid solution requires that the reaction be carried out at or near the boiling point of such solutions. Even under these conditions the reaction is sluggish and the end point is best determined potentiometrically. In this respect the determination is similar to the permanganate oxidation of the oxalate ion, except that in the latter case a potentiometric end point determination is not required. The oxidation of the oxalate ion has been carried out using the chlorocerate ion in hydrochloric acid solution as described by Willard and Young (4). In this case the reaction is not satisfactorily rapid at room temperature, but by employing iodine monochloride at a temperature of 50° C., the use of ferroin as indicator avoids the necessity for a potentiometric end point. This reaction is undesirably slow even at 50° C., which cannot be exceeded without destroying the ferroin indicator. The determination of the arsenite ion in sulfuric acid solution using the sulfato cerate ion has been described by Gleu (1). The reaction at ordinary temperatures is negligible unless osmic acid is present as catalyst. Ferroin is used as indicator and the reaction is inconveniently slow in the region of the equivalence point.

### Ferroin and Nitro-Ferroin as Indicators

Ferroin and nitro-ferroin as high-potential oxidation-reduction indicators, introduced by Waldeñ, Hammett, and Chapman (3), have transition potentials of 1.14 and 1.25 volts, respectively. Nitro-ferroin cannot be used successfully in sulfato cerate oxidimetry, since potentials of at least 1.55 to 1.6 volts are required, and for this reason it has not heretofore been employed in any practical quantitative application. For the same reason its use in nitrato and perchlorato cerate oxidimetry is very desirable. Fortunately, however, ferroin may be used with entirely satisfactory results, since nitro-ferroin is more expensive than ferroin from which it is prepared. Nitro-*o*-phenanthro-

TABLE I. COMPOSITION OF SOLUTIONS OF  $\text{Ce}(\text{ClO}_4)_6^{--}$  AND  $\text{Ce}(\text{NO}_3)_6^{--}$  STANDARDIZED

Solution No.	Cerate Ion Present	Acid Used	Method of Preparation	Cerate-Ion Concentration <i>N</i>	Remarks
1	$\text{Ce}(\text{ClO}_4)_6^{--}$	<i>N</i> $\text{HClO}_4$	Electrolytic	0.05624	Cerous-ion concentration practically nil
2	$\text{Ce}(\text{ClO}_4)_6^{--}$	3 <i>N</i> $\text{HClO}_4$	Electrolytic	0.05651	
3	$\text{Ce}(\text{ClO}_4)_6^{--}$	8 <i>N</i> $\text{HClO}_4$	Electrolytic	0.05440	
4	$\text{Ce}(\text{ClO}_4)_6^{--}$	4 <i>N</i> $\text{HClO}_4$	Electrolytic	0.09702	
5	$\text{Ce}(\text{NO}_3)_6^{--}$	<i>N</i> $\text{HNO}_3$	Electrolytic	0.05333	Solution contained small amounts of other cerium group metals
6	$\text{Ce}(\text{NO}_3)_6^{--}$	3 <i>N</i> $\text{HNO}_3$	Electrolytic	0.05146	
7	$\text{Ce}(\text{NO}_3)_6^{--}$	<i>N</i> $\text{HClO}_4$	$\text{K}_2\text{Ce}(\text{NO}_3)_6 + (\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	0.04269	Solution contained some free $\text{H}_2\text{Ce}(\text{NO}_3)_6$ , $\text{K}^+$ , $\text{NH}_4^+$ , and a small amount of other earths
8	$\text{Ce}(\text{NO}_3)_6^{--}$	<i>N</i> $\text{HClO}_4$	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	0.08320	
					Solution prepared from 96 per cent pure stock



line was found to have a melting point of 201.5° C. as contrasted with *o*-phenanthroline monohydrate, 99–100° C. The former dye base is light yellow in color and the latter pure white.

Determination of Oxalate and Arsenite

The preparation of perchlorato and nitrate cerate solutions has been described (2). The oxidation of sodium oxalate and sodium arsenite using the perchlorato cerate ions was carried out potentiometrically, using *N* perchloric acid solutions of the  $C_2O_4^{--}$  and  $AsO_3^{--}$  ions at room temperature. The same potentiometric assembly of apparatus was employed as that previously described (2). Nitro-ferroin was added as indicator to compare the visual and potentiometric end-point phenomena. The results are shown graphically in Figure 1.

The equivalence-point "break" in potential is 650 mv. in the case of the oxalate titration and 600 mv. in the case of the arsenite oxidation. Nitro-ferroin as indicator has its transition interval at an average potential of 1.25 volts, which corresponds to a value 0.11 volt higher than would be the case if ferroin were used. There is a noticeable advantage in the use of the former, since with ferroin a momentary preferential oxidation of the indicator occurs and a second or two is required for the pink color to return.

Standardization

Eight solutions of perchlorato and nitrate cerate in various concentrations of perchloric and nitric acids were prepared. The details of their preparation and composition are given in Table I.

SULFATO CERATE AND FERROUS SULFATE SOLUTIONS. An approximately 0.05 *N* solution of sulfato cerate ion was prepared by dissolving ceric sulfate in *N* sulfuric acid. A 10-liter solution of an approximately 0.05 *N* solution of ferrous sulfate in dilute sulfuric acid was prepared and stored under hydrogen to prevent change of titer. The sulfato cerate solution was compared with the ferrous sulfate solution and the ratio found to be 1.0248, the latter being somewhat stronger.

The sulfato cerate solution was then standardized by use of Bureau of Standards sodium oxalate which had been dried at 50° C. for 1 hour. An excess of the sulfato cerate solution was added to the sulfuric acid solution of weighed portions of the oxalate. The solutions were then heated to 50° C. for 5 minutes and after cooling were back-titrated, using the ferrous sulfate solution with ferroin as indicator. The results are shown in Table II.

TABLE II. STANDARDIZATION OF SULFATO CERATE SOLUTION USING SODIUM OXALATE

$Na_2C_2O_4$ Gram	$H_2Ce(SO_4)_3$ Taken Ml.	$FeSO_4$ Taken Ml.	$H_2Ce(SO_4)_3$ Required Ml.	Calculated Normality	Deviation from Average %
0.1132	50	14.82	34.81	0.04856	0.04
0.1092	50	15.97	33.63	0.04849	0.10
0.0883	50	22.29	27.16	0.04855	0.02
0.0958	50	20.04	29.46	0.04856	0.02
Av. 0.04854					0.045

From the results of Table II and the standard factor for the sulfato cerate solution, the ferrous sulfate solution is found to be 0.04974 *N*.

COMPARISON STANDARDIZATIONS. The eight cerate solutions described in Table I were now standardized, using weighed portions of U. S. Bureau of Standards sodium

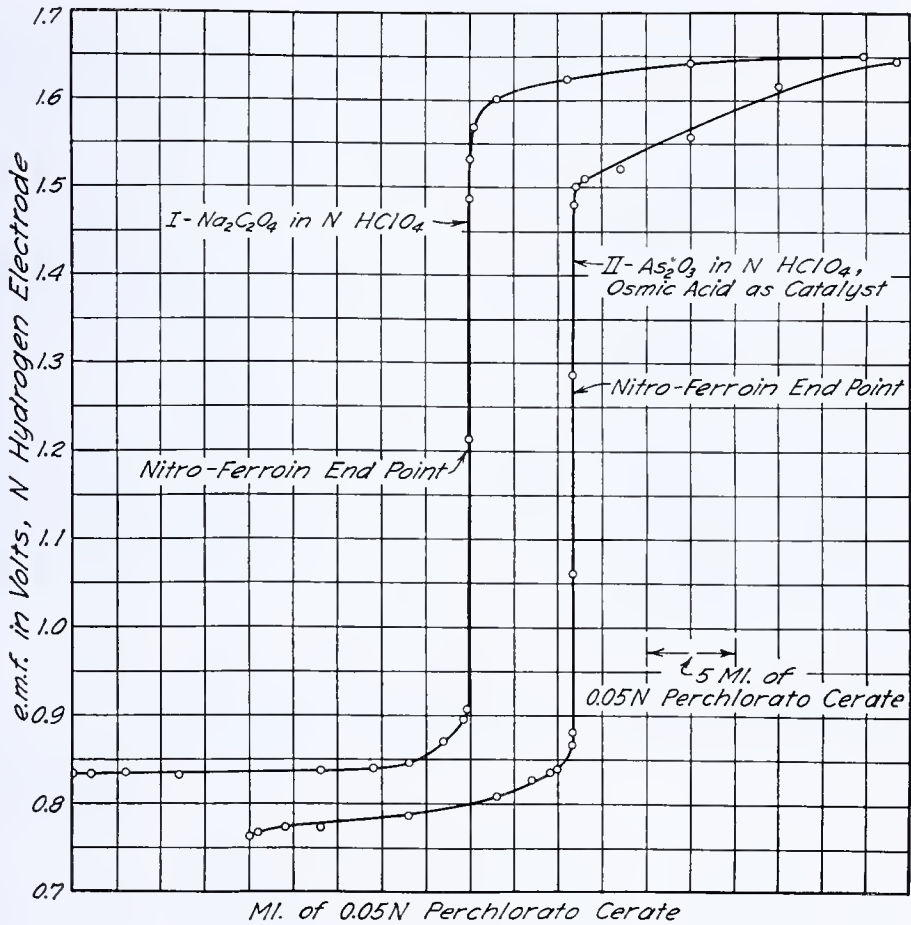


FIGURE 1

oxalate and arsenious oxide and measured volumes of standard ferrous sulfate.

TABLE III. STANDARDIZATION OF NITRATO AND SULFATO CERATE SOLUTIONS USING  $Na_2C_2O_4$ ,  $As_2O_3$ , and  $FeSO_4$

Solution No.	$Na_2C_2O_4$		$FeSO_4$		$As_2O_3$		Average Result <i>N</i>
	Factor <i>N</i>	No. of deter- mina- tions	Factor <i>N</i>	No. of deter- mina- tions	Factor <i>N</i>	No. of deter- mina- tions	
1	0.05624	5	0.05624	3	0.05627	4	0.05625
2	0.05642	6	0.05649	3	0.05663	5	0.05651
3	0.05439	7	0.05438	4	0.05442	4	0.05440
4	0.09700	7	0.09704	3	0.09746 <sup>a</sup>	6	0.09702
5	0.05333	4	0.05332	3	0.05344	4	0.05336
6	0.05147	6	0.05146	4	0.05147	5	0.05147
7	0.04274	5	0.04265	4	0.04267	5	0.04269
8	0.08313	4	...	...	0.08227	3	0.08220

<sup>a</sup> Omitted from average value for this solution.

All standardizations of a given cerate solution were carried out on the same day to eliminate the factor of possible instability of the various cerate solutions. In the case of sodium oxalate and arsenious acid the weighed portions were dissolved in 2 *N* perchloric acid before titration, and nitro-ferroin was used as indicator. The arsenious oxide was first dissolved in 1 gram sodium hydroxide, then acidified, and one drop of osmic acid as catalyst was added in the form of 0.01 *N* solution in 0.1 *N* sulfuric acid. In the case of the ferrous sulfate solutions, dilute sulfuric acid was added to give 1.5 *N* concentration at the time of titration and ferroin was used as indicator. In the case of the nitrate cerate solutions in nitric acid, the nitro-ferroin indicator reaction in the neighborhood of the equivalence point of the oxidation was not as satisfactory as in the absence of nitric acid but was still applicable. The results of the comparative standardizations are shown in Table III.

Discussion of Results

Table III shows a very satisfactory agreement between the values for the normality of perchlorato cerate and nitrate cerate solutions dissolved in nitric and perchloric acids of



various strengths as determined with sodium oxalate as standard when the same solutions are also standardized using ferrous sulfate. Since sodium oxalate is used as reference in both methods of standardization the results of the sulfato cerate procedure formerly used, with its much lower working potential, duplicate those of the perchlorato cerate procedure. Since ferroin was used with the sulfato cerate series and nitro-ferroin in the perchlorato cerate procedure, nitro-ferroin is shown to be equally well adapted to the higher potential oxidations. These are the first practical applications of nitro-ferroin as an indicator, since other lower potential oxidants have an appreciable titration error when used with this indicator.

The comparison of the normality of the various solutions as determined with sodium oxalate and ferrous sulfate and with arsenious acid is entirely satisfactory in all cases but two (solutions 4 and 8). The reason for the failure to obtain perfect agreement in these two cases is unknown but is postulated as due to a particular cerium group metal which is present in appreciable amount. The question is being investigated further.

Ammonium or potassium hexanitrate cerate was shown to be satisfactory for the preparation of the standard oxidizing solutions. Electrolytically oxidized cerate solutions were also found satisfactory.

### Summary

The potentiometric titration of the oxalate and arsenite ions in perchloric acid solution using perchlorato cerate solutions in perchloric acid has been made. A potential break of 650 and 600 mv., respectively, was obtained and nitro-

ferroin is shown to have a color transition point at the half-way interval of both potentiometric inflections.

The determination of the oxalate ion under the conditions indicated above has the advantage over permanganate and sulfato cerate that the reaction can be carried out at room temperature.

The determination of the arsenite ion in perchloric acid solution with osmic acid as catalyst and perchlorato cerate solutions as oxidant is more satisfactory than the corresponding determination in sulfuric acid solutions using sulfato cerate as oxidant.

Sodium oxalate, arsenious acid, and standard ferrous sulfate (standardized indirectly against oxalate) give concordant results in evaluating perchlorato or nitrate cerate solutions.

Nitro-ferroin (nitro-*o*-phenanthroline ferrous complex) has been used for the first time as an oxidation-reduction indicator. Its use in the case of perchlorate and nitrate cerate oxidations is practicable because of the high potential relationships involved in these cases. The transition from the reduced to the oxidized form of nitro-ferroin was found to be approximately 1.25 volts.

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# Chemical Studies of Wood Preservation

## The Wood-Block Method of Toxicity Assay

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**Actual decay resistance of treated wood is used as the basis for a simple laboratory technic in the assay of materials advocated for the protection of wood. In its present stage of development the test is a valuable tool in wood preservation studies.**

**E**XTENSIVE use of the more vulnerable species of timber for industrial purposes has focused attention on the development of technics for evaluating various preservatives advocated for the protection of this timber from the ravages of its natural enemies—fungi and termites. Using the substrate as a basis of classification, these technics fall roughly into two categories, nutrient agar tests exemplified by the Petri dish method as developed by the workers at the Forest Products Laboratory (4), and the wood-block test typified by the Kolle flask method (5), which has been widely used in Europe. The accumulation of toxicity data resulting from the use of both methods has received considerable study and the conclusions drawn by the various investigators have for the most part served only as a stimulus to controversies.

Discussion of the limitations of both methods in a previous paper (6) indicated the need for either modifying or supplanting these procedures. Both have at times been found to give misleading results which were detected only on actual exposure trials of corresponding materials. The principal shortcoming of the Petri dish method seems to be the artificial character of the dispersion of preservative in agar; that of the Kolle flask method the liability to inhibition of decay by excessive supply of water to the test block. The method described herein, slowly evolving during the course of the last 5 years, is an attempt to fulfill the requirements demanded of a laboratory technic for evaluating wood preservatives. It is felt that this test in its present stage of development combines the best features of the Petri dish and Kolle flask. The results to date show a much better correlation than those of either of the older methods with results of the more expensive and prolonged outdoor exposure tests.

While primarily intended for appraisal of preservatives, the method also lends itself to studies of rot-resistance of various woods, etc. Test blocks made from the heartwood and sapwood of many different species, from old poles which have been in service, from test posts (3), and from treated saplings (7) have yielded interesting information. Com-





FIGURE 1 (Left). APPARATUS  
REQUIRED FOR MODIFIED WOOD-BLOCK  
METHOD OF ASSAY



FIGURE 2 (Right).  
ASSEMBLY OF APPA-  
RATUS

mercially treated wood may be tested by the use of blocks cut from it, but in the majority of cases will not decay in the test unless the wood has been previously weathered artificially or naturally. However, most of the laboratory studies have been made on southern pine sapwood blocks impregnated with the preservative under test.

### Apparatus

Simplicity and low cost are obtained by using easily available apparatus.

Two sizes of bottles (\$0.12 per pair in gross lots), shown separately in Figure 1, are assembled as in Figure 2. The larger, screw-topped bottle (12 cm. high and 6 cm. in diameter) serves as a chamber in which moisture conditions optimal for decay are maintained. The smaller bottle (6 cm. high and 3 cm. in diameter) supports a thin slab of untreated sapwood ( $4.5 \times 2.5 \times 0.3$  cm., bored with two holes 0.5 and 0.2 cm. in diameter and approximately 1 cm. apart). The slab of sapwood acts as a substrate for growth of the fungus in a manner analogous to the artificial nutrient agar of the classical methods. The impregnated block under test is anchored upon the thin slab of sapwood by half-lengths of standard wooden applicators (16.5 cm. long) passed through holes bored in the slab and block.

After assembling the apparatus, water is added to the outer bottle to a depth of a few centimeters but not to the inner bottle. (Addition of the water to the small inner bottle is effected after sterilization to prevent the wood-cell vacuum formed during cooling from drawing up this water, thus saturating the piece to such an extent as to inhibit decay.) Sterilization is then effected by placing the complete setup in the autoclave for 30 minutes at 15 pounds' pressure. When the bottles have cooled sufficiently, sterile water is added to the inner bottle by means of a siphon arrangement. The additional moisture over that of fiber saturation which seems necessary for maximum decay is supplied to the fungus by conduction through the applicators. By means of a platinum spatula, previously flamed and cooled, a small inoculum is cut from a pure culture on agar of a wood-destroying fungus and is placed on the untreated slab at the end opposite the test block. The inoculation now completed, the bottles are recapped and placed in an incubation room at  $26^{\circ}$  to  $28^{\circ}$  C. for a period, customarily 24 weeks.

### Preparation of the Test Blocks

Care must be exercised in selecting wood for the test blocks. The wood, usually southern pine of the short-leaf type, must be of uniform growth rate, density, and ratio of springwood to summerwood. The presence of any heartwood, or of sapstain or other indication of incipient invasion by organisms, is sufficient reason for rejection. Blocks usually  $2 \times 2 \times 2$  cm. cut from such wood, bored with a hole 0.2 cm. in diameter

and numbered, are placed on racks (Figure 3) made from 1.25-cm. angle brass to which have been soldered finishing nails.

Some difficulty was experienced at first in the determination of the weights and volumes of the wood blocks. Weights taken at ordinary room conditions varied widely because of the moisture pickup of wood at different relative humidities. To avoid this, all blocks are brought to a constant relative humidity of 76 per cent at  $30^{\circ}$  C., which is obtained by fitting a bacteriological incubator with slow-moving fans and pans of saturated sodium chloride solution (Figure 4). Weighing the blocks is expedited by making initial weights at room conditions and properly arranging the blocks in order of either ascending or descending weight on the racks. The length of time required to reach equilibrium weights varies according to the amount of dry wood in the chamber and external atmospheric humidity, but the average period is from 3 to 4 days.

Volume determinations were first made by direct measurement with a micrometer, but this method was very slow and corrections for the hole could be only an approximation. A mercury-displacement method was devised which is far more precise and facile.

A 100-cc. beaker of mercury is placed on one pan of a rough balance and is counterpoised by weights on the other pan. The block is impaled on a dissection needle and forced beneath the surface of the mercury, care being taken that the block does not come into contact with the sides of the vessel holding the mercury. The force of the hand necessary to keep the block beneath the surface of the liquid is counterbalanced by additional weights on the opposite pan. (Experiments are now under way to devise a simple piece of apparatus to supplant the use of the hand in forcing the blocks beneath the mercury.) These weights, representing the weight of the mercury displaced, are then transposed into the volume of the block, correcting for the effect of temperature on the specific volume of mercury. Finally the blocks are brushed free of any mercury which might be retained on the

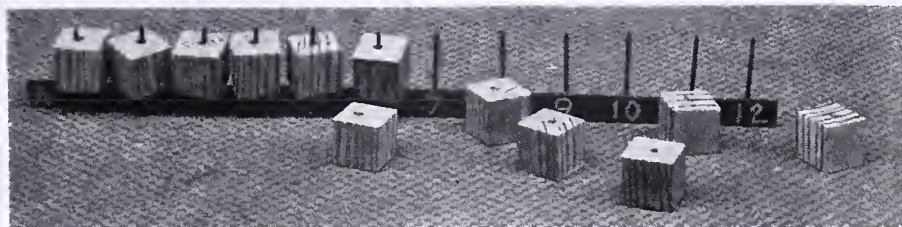


FIGURE 3. TEST BLOCKS AND RACK





FIGURE 4. CONSTANT-HUMIDITY CHAMBER FILLED WITH TEST BLOCKS

surface of the blocks; a final equilibrium weighing serves to detect such an occurrence.

### Treatment of the Test Blocks

The blocks are now ready for impregnation with the preservative to be tested. A considerable range of retents can be obtained by the use of the empty-cell process with the straight preservative, and while it is difficult to secure a predetermined range of concentration in this manner, the empty-cell process has been used to some extent in preparing test specimens. Since lower concentrations than those obtained with the undiluted preservative are often desirable, the proper amount of the compound to be tested is usually dissolved in an appropriate solvent. Usually a graded series of dilutions is desirable in order to approximate minimal effective concentration in at least one case.

The necessary number of blocks, weighted to ensure immersion, are placed in a container of convenient size under a bell jar fitted with a separatory funnel (Figure 5). After evacuation of the bell

jar to a pressure not greater than 2 cm. as measured by a mercury manometer, the vacuum is held for 5 minutes. The stopcock in the pump line is then closed and sufficient solution is admitted from the separatory funnel to submerge the blocks completely when the air is admitted. After remaining in the solution for a short time, the blocks are wiped superficially and weighed. This treated weight is used for calculation of the theoretical retent according to the following formula:

$$R = \frac{GC (62.5)}{100 V}$$

in which  $R$  = pounds per cubic foot,  $G$  = gain in weight in grams,  $C$  = grams of the preservative in 100 grams of solution, and  $V$  = volume of the test piece in cubic centimeters. When the solvent has evaporated from the blocks they are placed on the racks (Figure 3), returned to the humidity chamber, and again brought to constant weight. The difference between the humidity weights before and after treatment serves as the basis for calculating the actual retent and the final equilibrium weight is used also as the initial weight of the treated block before exposure to the fungus.

### Selection of Fungi

In each test at least four organisms from the following list are used in duplicate. The choice of each is based on their relative economic importance, the vigor of growth, amount of decay as measured by loss in weight of untreated specimens, and their known idiosyncracies for certain types of compounds. Another vital factor in the original selection of most of these fungi was their repeated isolation from de-



FIGURE 5. APPARATUS FOR FULL-CELL SOLUTION TREATMENTS OF TEST BLOCKS

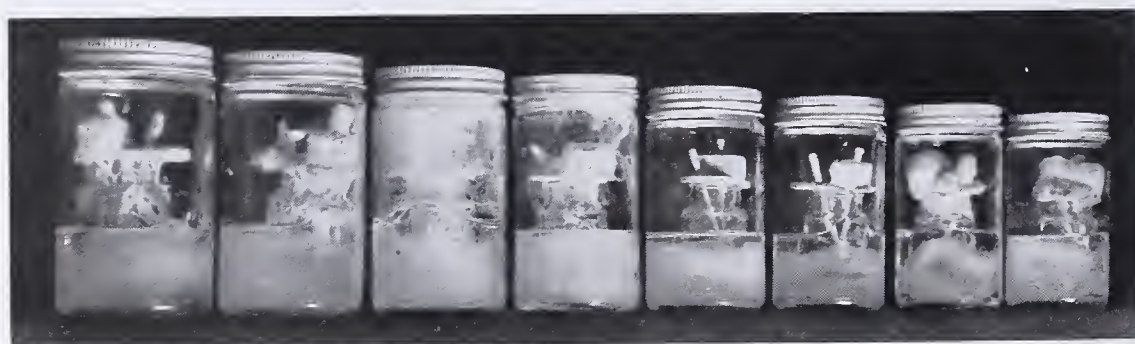


FIGURE 6. ASSAY OF WORTHLESS PRESERVATIVE AT MAXIMUM CONCENTRATION  
Fungi in duplicate, left to right, *Lenzites trabea*, U-10, *Fomes roseus*, and *Lentinus lepideus*

cayed pine poles sent in from widely separated areas.

Included in the list of fungi is *Lentinus lepideus*, which is used for the most part in the assay of organic preservatives but seldom for testing metallic salts, to which it is particularly sensitive. Similarly, the fungus *Lenzites trabea* exhibits a parallel resistance and sensitivity but the type





FIGURE 7. TOXICITY ASSAYS

Upper. Polychlorophenol, showing effect of increasing concentration. Test organism, *Lentinus lepideus*. Growth ratings, left to right, 4-4, 3-4, 1-3, and N. G. 4.

Center. Same range of concentration as in upper figure. Test organism, *Fomes roseus*. Growth ratings, left to right, 4-4, 4-4, 4-3, and 3-3.

Lower. Growth on untreated Baltic pine (*Pinus sylvestris*). Test organisms, *Lenzites trabea*, *Lentinus lepideus*, *Fomes roseus*, and U-10.

of rot differs greatly, producing a marked surface erosion of the blocks. The common "dry rot" fungi, specifically *Poria incrassata*, *Coniophora cerebella*, and *Polyporus vaporarius*, are most frequently used in the assay of inorganic compounds, since years of experimentation have demonstrated the relative resistance of these fungi to most such materials. *Fomes roseus*, another fungus of wide distribution, is able to withstand certain classes of compounds to a remarkable degree and hence is included in assays of all new compounds. One other organism (U-10) is used in all assays. Unfortunately, it has yet to be identified. Isolated several years ago from a decayed pine pole, U-10 is especially valuable when a quick indication of the merits of a new preservative is needed, as a very appreciable weight loss results from its attack in about 3 months. From time to time other organisms, such as *Trametes serialis*, *Lenzites sepiaria*, *Polystictus versicolor*, *Polyporus sulphureus*, *Fomes pinicola*, and other isolations from decayed poles and test posts (6) have supplemented the fungi regularly in use. Practically all of the above-mentioned have

been cited by investigators as of considerable economic importance in the decay of structural timbers.

### Expression of Results

The interpretation of results is greatly facilitated by proper controls, which include untreated blocks exposed to each of the test fungi and impregnated blocks put through the entire cycle without fungal inoculation. The untreated controls indicate the marked differences in the rapidity of growth and the amount of decay peculiar to various fungi on the species of wood being used. The impregnated controls serve as a check on the loss in weight due to leaching and evaporation occurring during the entire course of the test and are of further importance when the exposed blocks are dissected and rated on a strength basis. Using such controls three criteria are available:

1. The growth rating made every 4 weeks with reference to the inoculated untreated norm. The designation of growth is a pair of numbers, the first of which gives the extent of the block covered and the second the intensity and vigor. Based on "4-4" as the maximum, "2-4" would mean that the block is partly covered with normal growth of the fungal mycelium and "4-2" wholly covered with sparse mycelial growth. Additional designations to describe the absence of growth on the test specimens are used and include the "✓" mark when the inoculum is dead or totally inhibited and "N. G." for no growth on the test piece. A number following the latter designation indicates the extent of the growth on the untreated slab of supporting wood. The notation "N. G. 2" would mean that growth of the fungus has only partially covered the untreated wood used as the secondary substrate but is not yet in contact with the treated specimen. Such a notation is typical when there is some leaching of the preservative and attendant diffusion into the untreated slab.

2. The weight loss computed from the equilibrium weights before and after exposure to the fungus. Appreciable weight losses on the uninoculated, impregnated controls indicate that the preservative may be water-soluble, volatile, or reactive with the wood. Particularly when this latter condition prevails it is often difficult to distinguish the disintegration due to the chemical from the decay caused by the fungus, but the two effects can be separated by subtracting the per cent loss in weight calculated for the controls from the per cent loss in weight of the exposed specimens.

3. The third basis for judging the merits of a preservative is determined by dissecting and breaking the blocks into small pieces. The residual strength of the exposed blocks can thus be compared with the strength of the uninoculated, impregnated controls treated in the same manner. Dissection of the control also offers an indication of any chemical effect of the preservative on the wood. An empirical rating of 10 denotes no detectable loss in strength as compared to the control, and 0 denotes complete disintegration.

### Modifications and Special Features

While the assay method per se was not planned to include a test of permanency, correlative information in this regard



FIGURE 8. ASSAY OF FULL-CELL SOLUTION TREATMENT OF A CREOSOTE

Test organism, *Lenzites trabea*. Concentrations are, roughly, 1, 2, 3, and 6 pounds per cubic foot of creosote. Growth ratings, 4-4, 4-2, 3-1, and N. G. 1. For purposes of better reproduction inner bottles were removed from larger outer bottles.





FIGURE 9. INCUBATOR WITH TEST IN PROGRESS

on the more volatile preservatives may be obtained following the normal technic. Most of the solvents used in obtaining concentration ranges of oily preservatives are very toxic and considerable evaporation of high vapor pressure fractions is unavoidable not only during the evaporation of the solvent but also during the period while the test pieces are coming to constant weight in the humidity chamber and finally in connection with the sterilization. For instance, pieces treated with moderate amounts of a volatile material of known preservative value, such as naphthalene, when put through the regular routine showed no rot-resisting properties. Accordingly, whenever highly volatile compounds are under consideration, a generous quantity of the material is injected into the blocks to allow for partial evaporation. Actual retent can be calculated from the difference between the humidity weights of the untreated blocks and the weights of the impregnated blocks just prior to fungal exposure. Instead of subjecting blocks treated with volatile materials to sterilization, the technic is modified in a manner somewhat similar to the Kolle flask method. The fungus is first allowed to cover the untreated slab of sapwood for a period of 3 to 4 weeks before the specimens are treated. When the fungus is growing vigorously and no contaminations are apparent, the treated block, immediately after the final weighing, is placed in direct contact with the mycelial mats. A sterile applicator passed through the hole in the block is an aid in placing the block in position. When allowed to remain it ensures a sufficient supply of moisture to the test block.

The danger of foreign contaminations is heightened by omission of the sterilization, but in spite of this the results have been reasonably acceptable although somewhat irregular. This modification is far more satisfactory in the assays of single compounds than in assays of volatile mix-

tures. In both cases total evaporation is easily ascertained, but computation of the loss of each individual constituent of a mixture is practically impossible. Another method of avoiding the loss of volatile compounds is to place each weighed block in a small, tightly stoppered container during sterilization. Such a method is being more fully studied at this time.

When materials are known or suspected to be water-soluble, the injected blocks may be run through a standard leaching cycle before being subjected to the toxicity test. Or, in cases where the compounds are soluble and volatile, the specimens can first be exposed on artificial weathering machines such as were used by Rhodes *et al.* (1). If the preservative is likely to prove volatile but is inappreciably soluble, a standard heating cycle may be used. Such cycles give definite indication of the comparative values of preservatives from the standpoint of permanence. Indeed, many preservatives are so toxic that significant differences in toxicity among them often cannot be detected unless the blocks are first subjected to a depletion process imitative of the weather. As an alternate the blocks may be injected with very low concentrations as compared with those of commercial practice.

A standard leaching cycle which is dependent on diffusion and is to some extent a simulation of the action of ground waters on soluble materials injected into the wood is described below. Since the duplication of varied environmental factors in service is impossible, an arbitrary schedule was chosen which is adapted to usual working hours and is consistent with a minimum amount of supervision.

The individual impregnated blocks are numbered and then placed in the constant-humidity chamber (Figure 4) until an equilibrium weight is reached. All the blocks impregnated with the same preservative in equal concentration are then placed in a

TABLE I. AVERAGE WEIGHT LOSS BY KOLLE FLASK AND BELL TELEPHONE LABORATORIES METHOD

(Comparison of results on untreated *Pinus sylvestris* exposed to different fungi)

Organism	Strain	European Research Workers Using Kolle Flask				B. T. L. Method <sup>a</sup>	
		Baven- damm %	Liese %	Peters %	Ra- banus %	No. of speci- mens	Results %
<i>Polyporus vapori- arius</i>	Eberswalde	15	26	12	19	2	25.3
	Baarn	2	7	5	11	..	..
	Princes Risborough	..	8	6	10	..	..
<i>Lentinus lepideus</i>	Eberswalde	4	12	42	19	6	19.1
	Eberswalde	..	13	..	..	..	..
	Princes Risborough	3	12	21	14	..	..
	Princes Risborough	..	15	..	..	..	..
<i>Lenzites sepiaria</i>	Eberswalde	7	24	..	21	6	47.0
	Princes Risborough	5	19	..	14	..	..
	Madison	3	14	..	21	..	..
<i>Lenzites trabea</i>		..	..	..	..	6	35.2
U-10		..	..	..	..	6	43.2
<i>Fomes roseus</i>		..	..	..	..	4	22.2

<sup>a</sup> Strains of fungi, with the exception of U-10, used at Bell Telephone Laboratories were supplied by Forest Products Laboratory, Madison, Wis.

container of convenient size, weighted to ensure immersion during the early stages of the cycle, and covered with distilled water, allowing 50 cc. for each block (7 to 8 cc.). The containers are covered with a watchglass and set aside in a constant-temperature room at 26° to 28° C. The water is drained from the blocks and an equal amount of fresh water is again added at the end of



TABLE II. WEIGHT LOSSES AND DISSECTION RATINGS  
(Untreated southern pine blocks exposed to most common test fungi for 24 weeks)

Organism	Initial Weight	Final Weight	Empirical				Description of Decay
	76%	76%	Loss, Rating		Based Based		
	relative humidity	Oven-dry	relative humidity	Oven-dry	on Oven-Dry Weights %	on Dis-section	
	Grams	Grams	Grams	Grams			
<i>Lentinus lepideus</i>	2.34	2.05	1.87	1.64	20.0	4	Rather advanced decay throughout
	2.35	2.06	1.87	1.64	20.4	4	Rather advanced decay throughout
	2.25	1.97	1.85	1.62	17.8	5	Moderately advanced decay throughout
	2.26	1.98	1.77	1.55	21.7	4	Rather advanced decay throughout
<i>Fomes roseus</i>	2.25	1.97	1.84	1.61	18.3	4	Rather advanced decay throughout
	2.27	1.99	1.84	1.61	19.1	4	Rather advanced decay throughout
	2.22	1.95	1.78	1.56	20.0	4	Rather advanced decay throughout
	2.21	1.94	1.56	1.37	29.4	1	Thoroughly rotted
U-10	2.33	2.04	1.13	0.99	51.5	0	Complete disintegration
	2.33	2.04	1.37	1.20	41.2	0	Complete disintegration
	2.20	1.93	1.08	0.95	50.8	0	Complete disintegration
	2.18	1.91	1.19	1.04	45.5	0	Complete disintegration
<i>Lenzites trabea</i>	2.32	2.03	1.73	1.52	25.1	2	Deep surface disintegration, advanced decay elsewhere
	2.33	2.04	1.76	1.54	24.5	3	Deep surface disintegration, rather advanced decay elsewhere
	2.07	1.81	1.51	1.32	27.1	2	Advanced decay
	2.09	1.83	1.29	1.13	38.3	1	Thoroughly rotted
<i>Polyporus vaporarius</i>	2.12	1.86	1.69	1.48	20.4	4	Rather advanced decay throughout
	2.01	1.76	1.74	1.53	13.1	6	Mild decay throughout
	2.18	1.91	1.78	1.56	18.3	4	Rather advanced decay throughout
	2.26	1.98	1.82	1.60	19.2	4	Rather advanced decay throughout

Growth rating in all cases was 4-4, signifying that test blocks were covered with heavy normal growth.

the following periods: after a total of 7, 24, 48, 79, 168, and 336 hours. At the end of this 2-week period, the blocks are removed from the beakers; the water is allowed to evaporate after the blocks are placed on racks (Figure 3). The blocks are finally brought to a constant weight in the humidity chamber and run through the regular assay cycle. The weight before and after leaching is an indication of the amount of material lost through leaching. A further check is often made by analyzing the leach waters for the active constituents.

Results

Table I gives results by the new method on untreated *Pinus sylvestris* (Baltic or Scots pine) exposed to various fungi, compared with those of several other research workers (2) using the Kolle flask technic on the same species of wood. The agreement in general is very satisfactory. In the case of the fungus *Lenzites sepiaria*, the weight losses are about

double those of any other investigator, indicating that these test conditions are highly favorable for it. The results on this organism are the average of six individual blocks; the maximum weight loss was 50.6 per cent and the minimum 44.1 per cent. This is rather close agreement for biological test methods and is a good example of results obtained by this method. Although strictly comparable results are not available for the sapwood of the various species of southern yellow pine (*Pinus taeda*, *Pinus echinata*, *Pinus palustris*, and *Pinus caribaea*), the weight losses in Table II are in a general way typical of untreated wood of these species when assayed by the method described in this paper.

The gradual evolution of this laboratory assay to its present stage of development has been accompanied by the accumulation of a considerable mass of data on materials advocated for the preservation of wood. Since many of these compounds are of re-

cent acquisition, data for them which are comparable to those obtained by other investigators using the Kolle flask technic are as yet lacking. Some typical results are discussed below.

From a large number of creosotes tested, toxicity assays and chemical analysis of a random choice are given in Tables III, IV, and V. Results are for duplicate blocks at each concentration of the creosote in both full- and empty-cell treatment, together with duplicate blocks put through the standard leaching cycle referred to above. The resultant good agreement for duplicate blocks exposed to the same fungus is rather surprising, in view of the fact that evaporation losses are unavoidable when handling blocks impregnated with relatively volatile materials such as creosotes. When discrepancies arise, indications of the probable result may be obtained by comparison with the next higher or lower concentration, but the best policy is to make a duplicate test.

TABLE III. ASSAY OF CREOSOTE  
(Full-cell benzene solution treatment)

Concentration <i>Lb./cu. ft.<sup>a</sup></i>	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Lenzites trabea</i>			Uninoculated Control	
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	% loss	Dissection rating
6.6 Original	1-1	3.7	10	✓	3.8	10	✓	3.6	10	N. G. 2	3.9	10	3.7	10
	✓	3.8	10	✓	3.2	10	✓	3.1	10	N. G. 2	3.7	10	3.3	10
Leached	N. G. 4	2.5	10	1-1	1.8	10	2-1	1.4	10	N. G. 4 <sup>b</sup>	2.4	10	1.8	10
	1-1	2.0	10	1-1	1.6	10	3-3	0.9	10	N. G. 4 <sup>b</sup>	2.1	10	1.0	10
3.5 Original	4-1	2.7	10?	1-1	1.4	10	1-1	1.6	10	N. G. 1	1.1	10	1.2	10
	4-1	2.1	10?	1-1	1.0	10	1-1	1.0	10	N. G. 1	0.9	10	1.0	10
Leached	4-2	1.4	10?	3-4	6.3	8	4-4	13.0	6	3-2 <sup>b</sup>	7.9	8	0.8	10
	4-2	0.9	10?	4-2	1.4	9	4-4	3.0	9	2-2 <sup>b</sup>	3.1	9	0.5	10
1.7 Original	4-4	17.9	4	4-2	6.9	8	4-4	15.1	5	4-4	14.7	6	0.9	10
	4-2	2.1	9	2-2	6.3	8	4-4	8.9	7	4-3	10.4	7	0.5	10
Leached	4-4	10.0	7	4-4	9.8	7	4-4	7.4	7	4-3 <sup>b</sup>	10.7	7	0.3	10
	4-4	8.9	7	4-4	9.4	7	4-3	4.5	8	4-3 <sup>b</sup>	10.0	7	0.0	10
0.8 Original	4-4	16.9	4	4-4	7.9	7	4-4	11.5	6	4-4	16.3	5	0.9	10
	4-4	16.0	4	4-4	6.0	7	4-4	11.1	6	4-4	15.8	5	0.5	10
Leached	4-4	12.2	6	4-4	12.9	6	4-4	37.2	0	4-4 <sup>b</sup>	23.7	2	0.6	10
	4-4	11.2	6	4-4	9.7	7	4-4	22.0	2	4-4 <sup>b</sup>	21.2	2	0.0	10
0.4 Original	4-4	33.0	1	4-4	14.2	6	4-4	44.1	0	4-4	25.4	2	0.5	10
	4-4	29.7	1	4-4	3.8	8	4-4	39.7	0	4-4	22.2	2	0.0	10
Leached	4-4	16.1	5	4-4	22.3	3	4-4	47.7	0	4-4 <sup>b</sup>	16.6	4	0.7	10
	4-4	13.3	5	4-4	16.8	5	4-4	45.8	0	4-4 <sup>b</sup>	16.1	4	0.3	10

<sup>a</sup> 1 gram per 100 cc. equals 0.625 pound per cubic foot.  
<sup>b</sup> *Lenzites sepiaria* used in these cases.



TABLE IV. ASSAY OF CREOSOTE

(Empty-cell treatment)

Concentration Lb./cu. ft. <sup>a</sup>	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Lenzites trabea</i>			Uninoculated Control	
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	% loss	Dissection rating
8.1 Original	2-1	1.8	10	1-1	0.9	10	1-1	1.8	10	1-1	3.2	10	2.8	10
	1-1	1.6	10	1-1	0.4	10	1-2	0.5	10	2-1	3.2	10	2.2	10
Leached	1-1	3.6	10	N. G. 2	2.3	10	N. G. 1	2.3	10	N. G. 1	2.9	10	2.3	10
	1-1	2.7	10	N. G. 1	1.8	10	✓	3.1	10	N. G. 2	2.2	10	2.0	10
4.0 Original	3-1	1.3	10	2-1	0.9	10	1-1	0.5	10	2-2	5.1	9	0.8	10
	1-1	0.5	10	1-1	0.4	10	1-1	0.0	10	3-2	3.8	9	0.0	10
Leached	2-1	0.0	10	2-1	0.4	10	2-1	0.0	10	1-1	0.0	10	0.2	10
	2-1	0.0	10	2-1	0.0	10	2-1	0.0	10	N. G. 3	0.8	10	0.0	10
3.4 <sup>b</sup> Original	4-1	1.0	10	2-1	1.4	9	4-3	9.1	6	3-2	5.2	7	0.9	10
	4-1	0.4	10	2-1	0.0	10	4-2	6.1	7	2-1	4.9	8	0.3	10

<sup>a</sup> 1 gram per 100 cc. equals 0.625 pound per cubic foot.<sup>b</sup> Not enough of specimen available for leaching.

TABLE V. ANALYSIS OF CREOSOTE REFERRED TO IN TABLES III AND IV

(Analysis according to Bell Telephone Laboratories specification 6591)

Specific gravity at 38°/15.5° C.	1.063	
Water	Trace	
Distillation	%	
To 210° C.	0.00	
210-235° C.	10.30	white crystals
235-245° C.	12.75	pale yellow crystals
245-270° C.	22.83	yellow liquid + crystals 1 to 1
270-300° C.	15.79	brown liquid + yellow crystals
300-315° C.	7.63	lemon solid
315-355° C.	20.94	lemon solid
Residue	9.51	
Total	99.75	
Sulfonation residue (210-355° C., composite)	0.4 cc./100 grams	
Tar acids (210-355° C., composite)	5.4 cc./100 grams	
Benzene-insoluble	0.12%	
Coke test	0.44%	

Both here and in other laboratories considerable attention has been given to tetrachlorophenol in petroleum oil mixtures as possible wood preservatives, and the assay of a full-cell solution treatment of a 10 per cent mixture is illustrated in Table VI. The effect of leaching blocks treated with such a mixture is more noticeable than in the case of the creosote-treated blocks. Also of particular interest is the specificity of the fungus *Fomes roseus* towards this compound, which is typical of its reaction with related chlorophenols. Results of an empty-cell treatment of a 5 per cent solution of this compound are given in Table VII. As further depletion by leaching seems unnecessary, such a test was not made.

TABLE VI. ASSAY OF 10 PER CENT SOLUTION OF TETRACHLOROPHENOL IN PETROLEUM

(Full-cell benzene solution treatment)

Concentration Lb./cu. ft. <sup>a</sup>	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Lenzites trabea</i>			Uninoculated Control	
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	% loss	Dissection rating
6.9 Original	✓	4.4	10	N. G. 1	5.9	10	✓	4.1	10	✓	5.0	10	5.0	10
	✓	3.6	10	N. G. 3	5.9	10	✓	3.5	10	✓	4.5	10	5.8	10
Leached	N. G. 1	3.6	10	1-2	4.7	9	N. G. 2	3.2	10	1-1	3.8	10	3.8	10
	N. G. 1	2.7	10	1-1	4.0	9	✓	2.7	10	1-1	3.6	10	3.2	10
3.3 Original	N. G. 2	4.0	10	2-1	6.7	9	✓	2.6	10	✓	3.4	10	4.0	10
	N. G. 1	5.2	10	1-1	4.7	10	✓	2.5	10	✓	3.3	10	3.5	10
Leached	N. G. 3	2.4	10	3-4	14.7	5	N. G. 2	1.5	10	1-3	3.8	9	2.2	10
	N. G. 1	1.9	10	1-2	1.9	9	N. G. 1	1.7	10	1-3	3.6	9	2.0	10
1.6 Original	N. G. 4	3.3	10	4-4	14.2	6	N. G. 2	3.0	10	✓	2.2	10	3.0	10
	N. G. 3	3.1	10	4-4	12.1	7	1-1	2.7	10	✓	2.2	10	2.5	10
Leached	1-2	1.5	9	4-4	13.8	6	1-4	3.4	9	4-4	14.3	6	0.7	10
	N. G. 2	0.5	10	4-3	12.7	6	✓	0.4	10	2-3	8.1	7	0.5	10
0.8 Original	2-2	6.9	7	4-4	21.0	3	4-4	9.5	7	3-2	12.7	7	2.2	10
	1-2	2.7	9	4-4	18.5	3	4-4	5.5	8	N. G. 1	3.2	10	1.8	10
Leached	3-4	10.2	6	4-4	18.6	3	4-4	29.0	1	4-4	16.6	4	0.9	10
	3-4	8.3	7	4-4	15.3	4	4-3	2.3	9	4-4	15.5	4	0.5	10
0.4 Original	4-4	15.2	4	4-4	17.1	3	4-4	37.4	0	4-4	21.6	3	0.2	10
	4-3	9.6	6	4-4	15.9	3	4-4	25.8	1	4-4	19.4	3	0.0	10
Leached	4-4	16.0	4	4-4	15.0	3	4-4	44.9	0	4-4	25.7	1	0.0	10
	4-4	12.6	6	4-4	6.1	7	4-4	40.6	0	4-4	22.0	2	0.0	10

<sup>a</sup> 1 gram per 100 cc. equals 0.625 pound per cubic foot.

TABLE VII. ASSAY OF 5 PER CENT SOLUTION OF TETRACHLOROPHENOL IN PETROLEUM

(Empty-cell treatment)

Concentration Lb./cu. ft. <sup>a</sup>	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Lenzites trabea</i>			Uninoculated Control	
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	% loss	Dissection rating
5.1 Original	N. G. 3	5.0	10	4-3	9.6	7	✓	5.0	10	3-3	7.9	8	3.9	10
	1-1	4.7	10	4-3	9.3	7	✓	4.2	10	4-3	7.6	8	3.8	10
3.9 Original	1-1	2.7	10	4-4	21.5	3	N. G. 2	2.7	10	4-3	11.1	6	2.8	10
	1-1	2.7	10	4-4	14.6	5	✓	2.9	10	4-2	8.9	7	2.6	10
2.5 Original	1-2	2.8	9	4-4	17.2	5	✓	3.2	10	4-3	11.4	8	3.2	10
	1-1	3.3	10	4-4	8.2	8	✓	2.9	10	4-4	10.2	7	2.8	10

<sup>a</sup> 1 gram per 100 cc. equals 0.625 pound per cubic foot.



TABLE VIII. ASSAY OF A MIXTURE OF POTASSIUM DICHROMATE, SODIUM FLUORIDE, SODIUM ARSENITE, AND DINITROPHENOL  
(Full-cell water solution treatment. Assay made early in development of method. Duplicates and controls were not used.)

Concentration <i>Lb./cu. ft.<sup>a,b</sup></i>	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Polyporus vaporarius</i>		
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating
1.2 Original	N. G. 1	1.3	10	N. G. 3	1.0	10	N. G. 1	1.6	10	N. G. 1	1.2	10
Leached	1-4	0.3	10	4-4	0.3	10	1-4	3.0	9	4-4	6.4	7
0.6 Original	N. G. 3	0.9	10	N. G. 4	0.7	10	N. G. 4	0.5	10	✓	0.3	10
Leached	2-4	0.0	10	3-3	1.1	10	4-3	2.4	10	4-4	23.0	2
0.3 Original	N. G. 1	0.5	10	N. G. 4	0.7	10	N. G. 2	0.3	10	N. G. 3	0.4	10
Leached	1-4	0.5	10	4-3	+0.5	10	4-4	13.4	6	4-4	59.5	0
0.1 Original	N. G. 2	0.5	10	N. G. 4	0.0	10	N. G. 4	0.4	10	N. G. 4	0.2	10
Leached	4-4	5.3	7	4-4	4.9	7	4-4	39.1	0	4-4	8.0 <sup>c</sup>	7

<sup>a</sup> 1 gram per 100 cc. equals 0.625 pound per cubic foot.  
<sup>b</sup> Expressed in terms of dry salts.  
<sup>c</sup> Specimen saturated with water.

TABLE IX. ASSAY OF A MIXTURE OF ZINC CHLORIDE AND SODIUM DICHROMATE  
(Full-cell water solution treatment)

Concentration <i>Lb./cu. ft.<sup>a,b</sup></i>	<i>Poria incrassata</i>			<i>Coniophora cerebella</i>			U-10			<i>Polyporus vaporarius</i>			Uninoculated Control	
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	% loss	Dissection rating
2.2 Original	N. G. 2	2.6	10	1-1	2.9	10	N. G. 3	2.8	10	1-1	2.3	10	2.0	10
Leached	N. G. 2	1.4	10	1-1	1.6	10	N. G. 2	2.8	10	N. G. 3	1.5	10	2.3	10
	4-4	10.5	6	4-3	6.4	7	4-4	19.7	3	4-4	14.1	6	0.8	10
1.2 Original	2-4	3.3	8	4-3	5.0	7	4-4	19.6	3	4-4	11.3	6	0.4	10
	2-2	1.6	10	1-1	2.3	10	N. G. 3	0.0	10	3-3	4.2	9	0.9	10
Leached	N. G. 3	1.1	10	1-1	3.0	10	1-3	0.7	10	1-1	2.6	10	1.1	10
	4-4	9.7	6	4-3	10.8	6	4-4	34.4	0	4-4	32.2	1	0.5	10
0.7 Original	4-4	6.7	6	4-3	6.9	7	4-4	31.6	0	4-4	8.7	5	0.8	10
	N. G. 3	0.9	10	2-2	2.7	9	1-2	1.4	10	4-4	8.1	7	0.3	10
Leached	2-1	0.7	10	4-1	1.9	10	N. G. 4	0.5	10	4-2	3.4	9	0.0	10
	4-4	19.7	3	4-4	11.4	6	4-4	25.5	2	4-4	25.4	2	0.6	10
0.3 Original	4-4	15.2	4	4-4	10.9	6	4-4	12.0	6	4-4	17.4	4	0.2	10
	4-4	22.5	3	4-3	11.4	6	4-4	14.8	5	4-4	10.8	6	0.0	10
Leached	4-2	11.5 <sup>c</sup>	6	4-3	7.4	7	4-4	10.9	6	4-4	8.9	6	0.0	10
	4-4	11.4	6	4-3	14.0	5	4-4	24.7	2	4-4	16.5	4	0.0	10
0.2 Original	4-4	10.5	6	4-4	11.9	6	4-4	16.1	4	4-4	10.1	6	0.3	10
	4-4	28.6	1	4-2	12.0	6	4-4	31.9	0	4-4	8.6	6	0.2	10
Leached	4-4	24.6	2	3-2	11.3	6	4-4	12.9	6	4-4	8.2	6	0.0	10
	4-4	16.8	4	4-3	9.8	7	4-4	30.2	0	4-4	12.5	5	0.1	10
	4-4	14.1	5	4-3	9.6	7	4-4	23.8	2	4-4	8.9	6	0.0	10

<sup>a</sup> 1 gram per 100 cc. equals 0.625 pound per cubic foot.  
<sup>b</sup> Expressed in terms of dry salts.  
<sup>c</sup> Contamination present.

Two compounds of an inorganic nature are also included, a mixture of potassium dichromate, sodium fluoride, sodium arsenite, and dinitrophenol (Table VIII) and a mixture of zinc chloride and sodium dichromate (Table IX). Both products, especially the former, are reasonably effective before leaching but, from the appreciable decay found in several specimens subjected to the water cycle previously mentioned, it is obvious that in neither is there complete fixation of the toxic principles. Further indications that large amounts of the materials were extracted from the wood when in contact with water were obtained by analyzing the leach waters. However, both products represent a real advance in the search for a truly permanent water-borne preservative.

The assay in Table VIII was made during the evolutionary period of the method, as is evidenced by the use of single blocks and the lack of uninoculated controls. Two of the test organisms used at that time, *Lentinus lepideus* and *Fomes roseus*, were innocuous except at the very lowest concentration of the leached specimens. By the time the assay in Table IX was carried out it had been realized that these organisms were unsuitable for the evaluation of the inorganic type of preservatives and *Coniophora cerebella* and *Poria incrassata* had been substituted in such studies. That this was a happy choice is indicated by the extensive decay brought about by these fungi.

Discussion and Summary

An attempt at the reproduction of natural conditions in the laboratory is always attended by many difficulties, particularly when endeavoring to imitate biological phenomena in a state of dynamic equilibria. The laboratory method described in this paper, however, does have many features to recommend it:

1. The medium is the natural one.
2. The organisms are selected on the basis of their virulence in attacking the specific medium used and their resistance to the class of compounds under consideration.
3. Because of limiting factors inherent in organic systems, it is difficult to establish environmental optima for all the fungi, but for the most part the conditions of the test meet these criteria.
4. Each block has a specific identity, treatment, and case history.
5. The test furnishes important indications of the degree of permanence and other chemical properties of the preservatives as well as its toxicity.
6. Low-cost apparatus and a simple technic result in an inexpensive assay method, especially when compared with the more expensive outdoor exposure tests which can often be entirely eliminated in the case of unpromising materials.
7. Evidence is accumulating from correlated field-exposure tests which indicates a high degree of specificity for the method.



8. While results on quadruplicate untreated blocks (Table II) and duplicate treated blocks show good agreement, data on reproducibility of this technic in other hands are not available at the present time, and definite claims for the true reproducibility of the method must await trial by other workers.

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# Thermal Conductivity of Liquids

## Binary Mixtures of Water-Methyl Alcohol and Water-Ethyl Alcohol

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The paper presents improvements in the operation of the apparatus previously reported (1, 2), and the results of the determinations of the thermal conductivity and temperature coefficients of thermal conductivity for water-methyl alcohol and water-ethyl alcohol binary mixtures.

BATES reported in detail the method of determining the thermal conductivity of liquids, a description of the apparatus, and the calculation of the coefficients in previous papers (1, 2). Figure 1 gives a general view of the present setup. However, two changes have been made in the operation of the apparatus from that previously reported.

To minimize conduction from the room to the calorimeters, the calorimeter water must be kept at room temperature, besides insulating heavily with rock wool and magnesia insulation. During the winter months electrical heating of the calorimeter cooling water from 5° to 20° C. requires the continuous use of about 2 kilowatts. To reduce the power consumption and eliminate the necessity for thermostatic controls, the authors recirculated the cooling water, taking special care to keep the temperature constant.

A small centrifugal pump (B, Figure 2) delivered the cooling water from the calorimeters back to the constant-head tank, located some 2 meters (6 feet) above the apparatus. To prevent vibration from reaching the apparatus, the pump was cushioned by several inches of sponge rubber, and all piping insulated from the walls by sponge rubber. Cold water from the secondary constant-head tank (C, Figure 2) was added to the circulating water at an open tank at the inlet to the pump, to balance the heat picked up in passing through the calorimeters. A specially constructed needle valve in the outlet of the secondary constant-head tank accurately controlled the amount of water added. In this manner, the temperature of the test calorimeter was maintained very steadily. Since the work requires equilibrium temperature conditions, this method of controlling the temperature of the water flowing through the calorimeters seemed superior to electrical heating and thermostatic control.

The line voltage must be controlled very closely to eliminate fluctuations of the heater temperature. A 250-watt Raytheon voltage

regulator (A, Figure 2) provided a completely constant voltage and, with the recirculating water system described above, virtually eliminated temperature fluctuations of the apparatus.

### Procedure

A previous paper (1) explained in detail the experimental procedure and method of calculation of the various coefficients. The values of the several coefficients were calculated from the temperature gradient curves drawn for each series of runs. In this case, a series of tests was made for liquid mixtures of the following compositions (in per cent by weight):

#### Methanol-Water

Distilled water

9.0 per cent methanol-91.0 per cent water  
18.4 per cent methanol-81.6 per cent water  
35.8 per cent methanol-64.2 per cent water  
58.0 per cent methanol-42.0 per cent water  
77.1 per cent methanol-22.9 per cent water  
89.2 per cent methanol-10.8 per cent water  
99.4 per cent methanol- 0.6 per cent water

The methanol was received from E. I. du Pont de Nemours & Co., Inc. The composition was reported as 99.85 per cent or better, and the specific gravity given as 0.79620 at

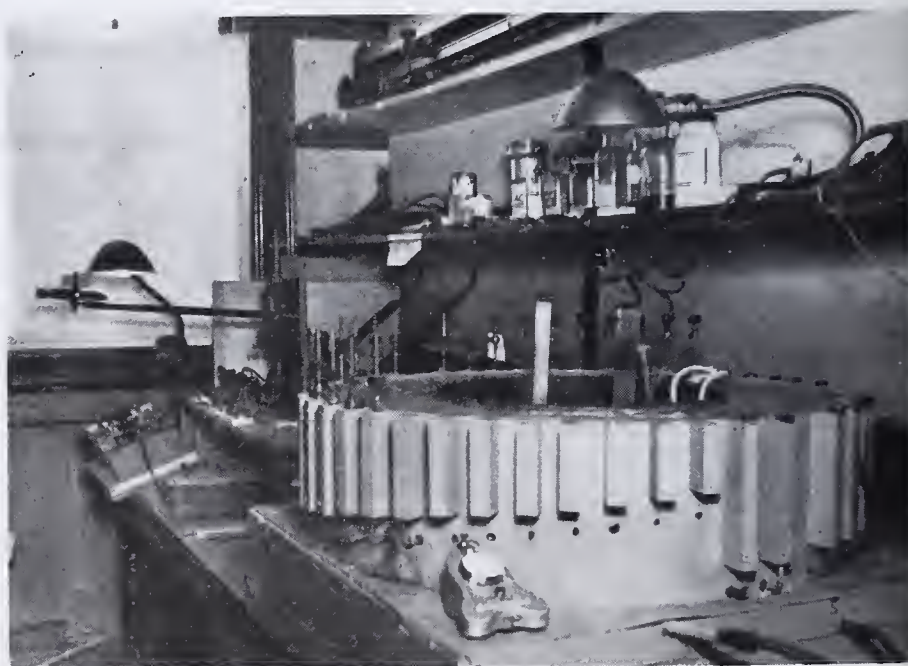


FIGURE 1. GENERAL LAYOUT OF APPARATUS



TABLE I. TRUE COEFFICIENT OF THERMAL CONDUCTIVITY ( $K_t$ )

Water	Methanol	Values of $K_t$							$\alpha_{20}^b$ %, ° C. <sup>-1</sup>	Equations for True Coefficient of Thermal Conductivity
		10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.		
% by weight		Gram calories, second <sup>-1</sup> , cm. <sup>-2</sup> , ° C. <sup>-1</sup> , cm. <sup>a</sup>								
100	(Pure water)	0.00138	0.00141	0.00145	0.00149	0.00152	0.00156	0.00160	0.27	$K_t = 0.00134 + 0.00000365 (t)$
95	5	0.00132	0.00135	0.00139	0.00142	0.00146	0.00149	0.00151	0.26	$K_t = 0.00128 + 0.00000350 (t)$
90	10	0.00126	0.00129	0.00132	0.00135	0.00139	0.00142	0.00145	0.25	$K_t = 0.00123 + 0.00000315 (t)$
85	15	0.00120	0.00123	0.00126	0.00129	0.00132	0.00134	0.00137	0.22	$K_t = 0.00118 + 0.00000275 (t)$
80	20	0.00115	0.00117	0.00120	0.00122	0.00125	0.00127	0.00129	0.21	$K_t = 0.00113 + 0.00000225 (t)$
75	25	0.00110	0.00112	0.00114	0.00116	0.00118	0.00120	0.00122	0.18	$K_t = 0.00108 + 0.00000200 (t)$
70	30	0.00105	0.00107	0.00108	0.00110	0.00112	0.00113	0.00115	0.14	$K_t = 0.00103 + 0.00000175 (t)$
65	35	0.00100	0.00101	0.00103	0.00104	0.00105	0.00106	...	0.12	$K_t = 0.00099 + 0.00000125 (t)$
60	40	0.00096	0.00096	0.00097	0.00098	0.00099	0.00100	...	0.10	$K_t = 0.00095 + 0.00000075 (t)$
55	45	0.00091	0.00092	0.00092	0.00093	0.00093	0.00094	...	0.06	$K_t = 0.00091 + 0.00000050 (t)$
50	50	0.00088	0.00088	0.00088	0.00088	0.00088	0.00088	...	0.00	$K_t = 0.00088$
45	55	0.00083	0.00083	0.00083	0.00082	0.00082	0.00082	...	-0.03	$K_t = 0.00083 - 0.00000025 (t)$
40	60	0.00079	0.00079	0.00078	0.00078	0.00077	0.00077	...	-0.06	$K_t = 0.00080 - 0.00000050 (t)$
35	65	0.00076	0.00075	0.00074	0.00073	0.00072	0.00072	...	-0.10	$K_t = 0.00076 - 0.00000075 (t)$
30	70	0.00072	0.00071	0.00070	0.00069	0.00068	0.00067	...	-0.11	$K_t = 0.00073 - 0.00000100 (t)$
25	75	0.00069	0.00067	0.00066	0.00065	0.00064	...	...	-0.11	$K_t = 0.00070 - 0.00000125 (t)$
20	80	0.00065	0.00064	0.00062	0.00061	0.00060	...	...	-0.16	$K_t = 0.00066 - 0.00000125 (t)$
15	85	0.00062	0.00060	0.00059	0.00058	0.00056	...	...	-0.17	$K_t = 0.00063 - 0.00000125 (t)$
10	90	0.00059	0.00057	0.00056	0.00054	0.00053	...	...	-0.18	$K_t = 0.00060 - 0.00000150 (t)$
5	95	0.00055	0.00054	0.00052	0.00051	0.00050	...	...	-0.19	$K_t = 0.00057 - 0.00000150 (t)$
(Pure methanol)	100	0.00053	0.00051	0.00050	0.00048	0.00047	...	...	-0.20	$K_t = 0.00054 - 0.00000150 (t)$

<sup>a</sup>  $K_t$ (cal., sec.<sup>-1</sup>, cm.<sup>-2</sup>, ° C.<sup>-1</sup>, cm.) 2900 =  $K_t$ (B. t. u., hr.<sup>-1</sup>, ft.<sup>-2</sup>, ° F.<sup>-1</sup>, inch).

C. g. s. system, English system

<sup>a</sup>  $K_t$ (cal., sec.<sup>-1</sup>, cm.<sup>-2</sup>, °C.<sup>-1</sup>, cm.) 2900 =  $K_t$ (B. t. u., hr.<sup>-1</sup>, ft.<sup>-2</sup>, °F.<sup>-1</sup>, inch).  
C. g. s. system, English system

<sup>b</sup>  $\alpha_{20}$  as defined by  $K_t = K_{20}[1 + \alpha_{20}(t - 20)]$ .

TABLE II. TRUE COEFFICIENT OF THERMAL CONDUCTIVITY ( $K_t$ )

Water % by weight	Ethyl Alcohol	Values of $K_t$						$\alpha_{20}^b$ %, °C. <sup>-1</sup>	Equations for True Coefficient of Thermal Conductivity
		10° C.	20° C.	30° C.	40° C.	50° C.	60° C.		
		Gram calories, second <sup>-1</sup> , cm. <sup>-2</sup> , °C. <sup>-1</sup> , cm. <sup>a</sup>							
100	(Pure water)	0.00138	0.00141	0.00145	0.00149	0.00152	0.00156	0.27	$K_t = 0.00134 + 0.00000365 (t)$
95	5	0.00131	0.00135	0.00139	0.00142	0.00145	0.00149	0.25	$K_t = 0.00128 + 0.00000335 (t)$
90	10	0.00125	0.00128	0.00132	0.00135	0.00138	0.00141	0.23	$K_t = 0.00122 + 0.00000300 (t)$
85	15	0.00119	0.00122	0.00125	0.00128	0.00130	0.00133	0.22	$K_t = 0.00116 + 0.00000270 (t)$
80	20	0.00113	0.00116	0.00119	0.00121	0.00123	0.00126	0.21	$K_t = 0.00111 + 0.00000245 (t)$
75	25	0.00108	0.00110	0.00112	0.00114	0.00116	0.00118	0.18	$K_t = 0.00106 + 0.00000200 (t)$
70	30	0.00102	0.00104	0.00106	0.00107	0.00109	0.00110	0.16	$K_t = 0.00101 + 0.00000165 (t)$
65	35	0.00097	0.00098	0.00099	0.00101	0.00102	0.00103	0.14	$K_t = 0.00095 + 0.00000130 (t)$
60	40	0.00092	0.00093	0.00093	0.00094	0.00095	0.00096	0.11	$K_t = 0.00091 + 0.00000100 (t)$
55	45	0.00087	0.00087	0.00088	0.00088	0.00089	0.00089	0.08	$K_t = 0.00086 + 0.00000070 (t)$
50	50	0.00082	0.00082	0.00083	0.00083	0.00083	0.00083	0.04	$K_t = 0.00082 + 0.00000030 (t)$
45	55	0.00078	0.00077	0.00077	0.00077	0.00077	0.00077	0.00	$K_t = 0.00078$
40	60	0.00073	0.00073	0.00072	0.00072	0.00072	0.00071	-0.05	$K_t = 0.00074 - 0.00000035 (t)$
35	65	0.00069	0.00068	0.00068	0.00067	0.00066	0.00066	-0.10	$K_t = 0.00070 - 0.00000070 (t)$
30	70	0.00065	0.00064	0.00063	0.00062	0.00061	0.00060	-0.16	$K_t = 0.00067 - 0.00000115 (t)$
25	75	0.00062	0.00061	0.00059	0.00058	0.00057	0.00056	-0.22	$K_t = 0.00063 - 0.00000130 (t)$
20	80	0.00058	0.00057	0.00055	0.00054	0.00052	0.00051	-0.25	$K_t = 0.00059 - 0.00000140 (t)$
15	85	0.00055	0.00053	0.00051	0.00050	0.00048	0.00046	-0.32	$K_t = 0.00056 - 0.00000170 (t)$
10	90	0.00052	0.00050	0.00048	0.00046	0.00044	0.00042	-0.40	$K_t = 0.00054 - 0.00000200 (t)$
5	95	0.00049	0.00047	0.00044	0.00042	0.00040	0.00038	-0.48	$K_t = 0.00052 - 0.00000235 (t)$
(Pure ethyl)	100	0.00046	0.00043	0.00041	0.00038	0.00036	0.00033	-0.54	$K_t = 0.00048 - 0.00000250 (t)$

$\alpha K_t(\text{cal., sec.}^{-1}, \text{cm.}^{-2}, \text{°C.}^{-1}, \text{cm.}) 2900 = K_t(\text{B. t. u., hr.}^{-1}, \text{ft.}^{-2}, \text{°F.}^{-1}, \text{inch}).$

C. g. s. systemEnglish system

<sup>a</sup>  $K_t$ (cal., sec.<sup>-1</sup>, cm.<sup>-2</sup>, °C.<sup>-1</sup>, cm.) 2900 =  $K_t$ (B. t. u., hr.<sup>-1</sup>, ft.<sup>-2</sup>, °F.<sup>-1</sup>, inch).  
C. g. s. system, English system

<sup>b</sup>  $\alpha_{20}$  as defined by  $K_t = K_{20}[1 + \alpha_{20}(t - 20)]$ .

15° C./4° C. The distillation range did not exceed 1° C. from first drop to dry on an Engler distillation unit.

Ethyl Alcohol-Water

Distilled water

- 11.0 per cent ethyl alcohol-89.0 per cent water
- 20.2 per cent ethyl alcohol-79.8 per cent water
- 37.4 per cent ethyl alcohol-62.6 per cent water
- 64.9 per cent ethyl alcohol-35.1 per cent water
- 79.2 per cent ethyl alcohol-20.8 per cent water
- 91.7 per cent ethyl alcohol- 8.3 per cent water

The ethyl alcohol used was 190 proof industrial alcohol U. S. P., manufactured by the U. S. Industrial Alcohol Co.

From the calorimetric determinations and the temperature gradient curves, the true thermal conductivities were determined for the binary liquid mixtures listed above over the range of temperature covered for the particular runs. In every case, within the accuracy of the tests, the true thermal conductivity was a linear function of the temperature—that is, a straight-line relation. From these curves, composition

vs. true thermal conductivity curves were drawn for every 10° C. interval.

True Thermal Conductivity,  $K_t$

The final data given in Tables I and II and graphically in Figures 3, 4, 5, and 6 were obtained from the conductivity-composition curves. By means of either the tables or the graphs it is possible to determine the true thermal conductivity of binary liquid mixtures of both methanol-water and ethyl alcohol-water for any temperature from 10° to 70° C. and for any composition from distilled water to pure alcohol.

Average or Mean Thermal Conductivity

The average thermal conductivity,  $K_t^2$  between any two temperatures,  $t_2$  and  $t_1$ , covered by the experiments and for any composition, can also be readily determined by using the average or mean temperature from Tables I and II and Figures 3, 4, 5, and 6. Since the true thermal conductivity is a linear



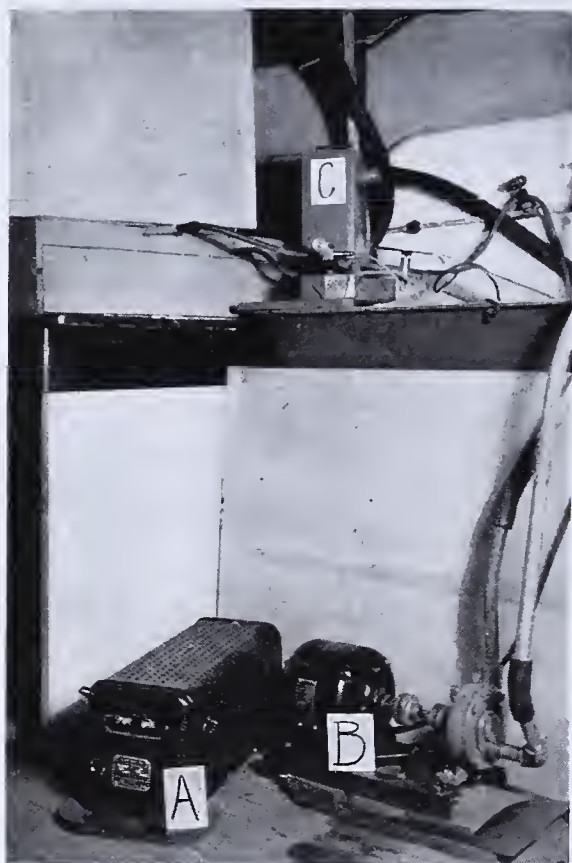


FIGURE 2. VOLTAGE REGULATOR, A, CENTRIFUGAL PUMP, B, AND SECONDARY CONSTANT-HEAD TANK, C

function of the temperature, the average thermal conductivity between temperatures  $t_2$  and  $t_1$  must be the same as the true coefficient at  $\frac{t_2 + t_1}{2}$  or the average of the two temperatures.

### Discussion of Results

The thermal conductivity values calculated from new tests run on redistilled water checked with the results given by Bates in 1936 (2). His investigation was carried on with the same apparatus, but at the Massachusetts Institute of Technology, with electrically heated, thermostatically controlled calorimeter water.

Results for both binary mixtures (methanol-water and ethyl alcohol-water) show a temperature coefficient which reduces to zero at approximately a 50 per cent solution, going negative for alcohol concentrations higher than 50 per cent. In other words, the temperature coefficient of thermal conductivity is positive for distilled water ( $\alpha_{20} = +0.26\%$ ,  $^{\circ}\text{C}^{-1}$ ), approaches zero at 50 per cent methanol-50 per cent water, and is negative for pure methanol ( $\alpha_{20} = -0.20\%$ ,  $^{\circ}\text{C}^{-1}$ ). For ethyl alcohol-water mixtures the zero coefficient occurs around 52 per cent ethyl alcohol-48 per cent water, and is negative for pure ethyl alcohol ( $\alpha_{20} = -0.54\%$ ,  $^{\circ}\text{C}^{-1}$ ).

Table III gives a comparison of the thermal conductivity values for water, methanol, and ethyl alcohol with those found by other observers.

Barratt and Nettleton in the International Critical Tables proposed an equation for cal-

culating the true thermal conductivity of binary liquid mixtures when the conductivities of the two liquids are known. The equation is

$$K \sinh(100\mu) = K_1 \sinh(p_1\mu) + K_2 \sinh(p_2\mu)$$

"where  $p_1$  and  $p_2$  are the percentages by weight of the two constituents and  $\mu$  is a constant depending upon the constituents and the temperature." The following is a sample calculation using the above equation:

Calculation of the thermal conductivity of a 40 per cent ethyl alcohol-60 per cent water binary mixture at  $20^{\circ}\text{C}$ .

$$\begin{aligned} p_1 &= 40, p_2 = 60 \\ K_1 &= 0.00043, K_2 = 0.00141 \text{ (Table II)} \\ 100\mu &= 0.94 \end{aligned}$$

TABLE III. COMPARISON OF VALUES FOR TRUE THERMAL CONDUCTIVITY OF WATER, METHYL ALCOHOL, AND ETHYL ALCOHOL

Liquid	Observer	Year	$K_t^a$ (True)	Temperature, $^{\circ}\text{C}$ .	$\alpha_{20}^b$ (%, $^{\circ}\text{C}^{-1}$ )
Water	I. C. T. (3)	1929	0.00138	20	0.28
	Bates (2)	1936	0.00141	20	0.26
	Bates, Hazzard, Palmer	1938	0.00141	20	0.26
Methyl alcohol	I. C. T.	1929	0.00050	20	-0.053
	Bates, Hazzard, Palmer	1938	0.00051	20	-0.20
Ethyl alcohol	I. C. T.	1929	0.000435	20	-0.071
	Bates, Hazzard, Palmer	1938	0.00043	20	-0.54
	Schack (5)	1933	0.00041	40	....
	Saha and Srivastava (4)	1931	0.00043	25	....

<sup>a</sup> Units of  $K_t$  = gram cal., sec.<sup>-1</sup>, cm.<sup>-2</sup>,  $^{\circ}\text{C}^{-1}$ , cm.

<sup>b</sup>  $\alpha_{20}$  as defined by  $K_t = K_{20} [1 + \alpha_{20}(t - 20)]$ .

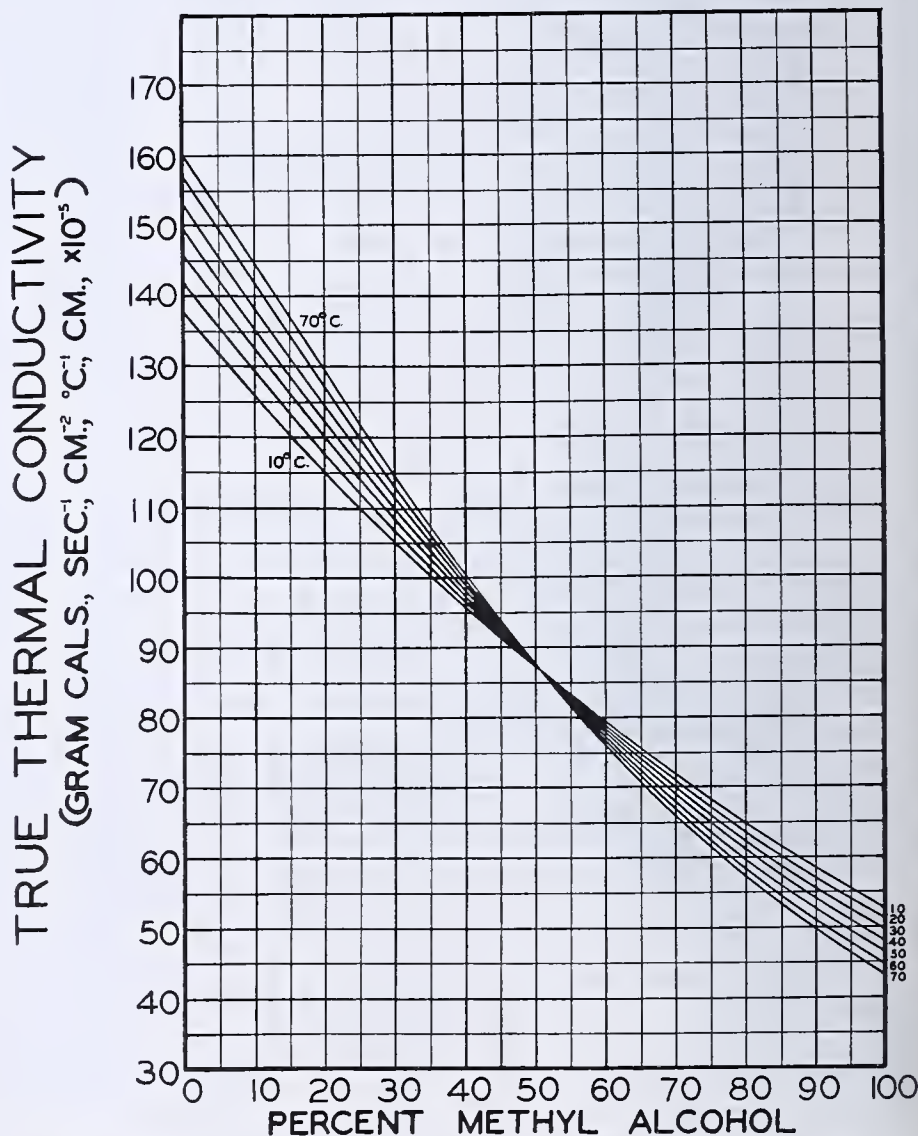


FIGURE 3. THERMAL CONDUCTIVITY-COMPOSITION CURVES FOR METHYL ALCOHOL-WATER SOLUTIONS



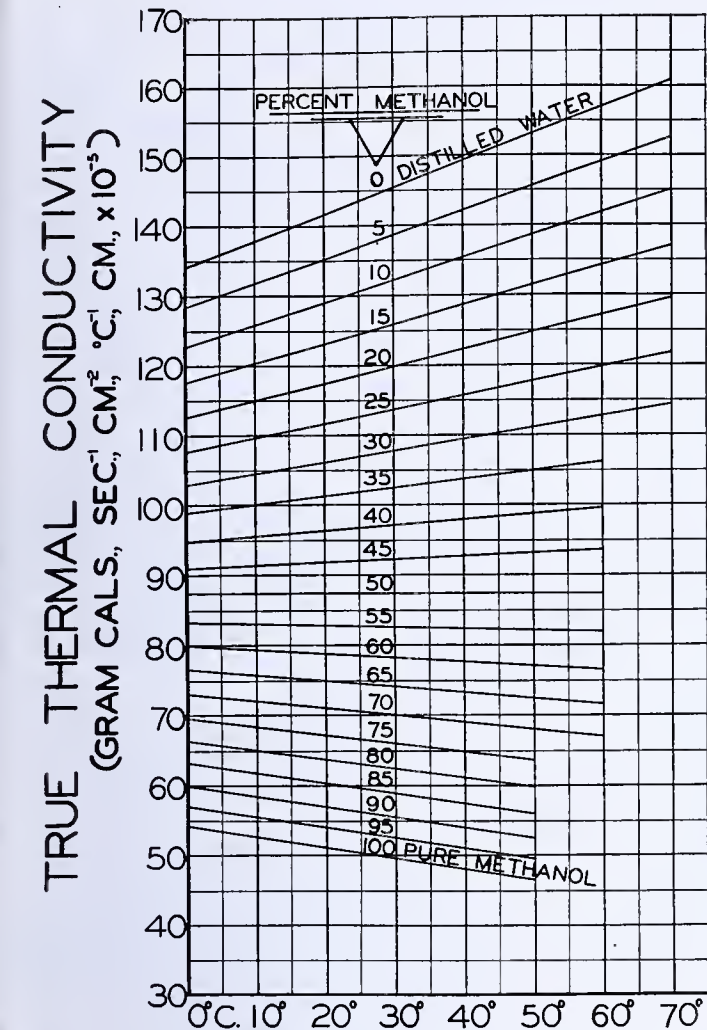


FIGURE 4. THERMAL CONDUCTIVITY-TEMPERATURE CURVES FOR METHYL ALCOHOL-WATER SOLUTIONS

Therefore,

$$K = \frac{0.00043 \sinh (40 \times 0.0094) + 0.00141 \sinh (60 \times 0.0094)}{\sinh (0.94)}$$

From a table of hyperbolic sines, we get:

$$\sinh 0.94 = 1.085, \sinh 0.376 = 0.385, \sinh 0.564 = 0.594$$

Substituting these values and solving,

$$K = 0.000925$$

Using the authors' values of  $K_i$  and values of  $\mu$  given in the International Critical Tables (3), they found variations of 5

TABLE IV. COMPARISON OF OBSERVED THERMAL CONDUCTIVITIES WITH CONDUCTIVITIES COMPUTED FROM EQUATION  $K \sinh (100 \mu)=K_1 \sinh \left(p_1 \mu\right)+K_2 \sinh \left(p_2 \mu\right)$

Water Solutions of	Composi- tion % by weight	$K_{obs.}$ at 20° C.	$K_{calc.}$ at 20° C. <sup>a</sup>	$\Delta \times 10^{-5}$	$K_{calc.}$ at 20° C. <sup>b</sup>	$\Delta \times 10^{-5}$
Ethyl alcohol	20	0.00116	0.00109	7	0.00115	1.0
	40	0.00093	0.00084	9	0.000925	0.5
	60	0.00073	0.00066	7	0.000735	-0.5
	80	0.00057	0.00053	4	0.00057	0
Methyl alcohol	20	0.00117	0.00111	6	0.001175	-0.5
	40	0.00096	0.00088	8	0.00096	0
	60	0.00079	0.00071	8	0.00079	0
	80	0.00064	0.00059	5	0.00064	0
Glycerol <sup>c</sup>	20	0.00124	0.00125	-1	0.001215	2.5
	40	0.00107	0.00111	-4	0.001065	0.5
	60	0.00091	0.00095	-4	0.00092	-1.0
	80	0.00078	0.00081	-3	0.000795	-1.5

<sup>a</sup>  $K_{calc.}$  is obtained from the above equation using values of  $100 \mu_{20}$  for ethyl alcohol = 1.34, for methyl alcohol = 1.30, and for glycerol = 0.40 as given in International Critical Tables.  
<sup>b</sup>  $K_{calc.}$  is obtained from the above equation using values of  $100 \mu_{20}$  for ethyl alcohol = 0.94, for methyl alcohol = 0.90, and for glycerol = 0.65 as determined by the authors.  
<sup>c</sup> Values for  $K_i$  of glycerol were obtained from (2).  
 $\Delta = K_{obs.} - K_{calc.}$

to 10 per cent of the calculated  $K_i$  from the observed  $K_i$  (Table IV). However, since the residuals ( $\Delta$ ) were all of the same sign, it seemed necessary to change only  $\mu$  to make the equation fit. When  $\mu$  is changed to make the sum of the residuals ( $\Delta$ ) as small as possible, the equation fits the data very well. On the basis of the above calculations, the authors suggest the following values of  $100 \mu$  at 20° C.: ethyl alcohol = 0.94, methyl alcohol = 0.90, glycerol = 0.65.

The International Critical Tables suggest that  $\mu$  is a function of the temperature but give only the value at 20° C. Values of  $K_i$  calculated for higher temperatures, the authors' values for  $100 \mu_{20}$  suggested above being used, showed fairly good agreement with observed conductivities at those temperatures. Since the agreement up to 80° C. is good (Table V), it would seem useless to change  $\mu$  at higher temperatures,

TABLE V. COMPARISON OF OBSERVED AND COMPUTED VALUES OF  $K_i$

(Showing the degree of independence of  $\mu$  with temperature)

Water Solutions of	Composi- tion % by weight	Tempera- ture ° C.	$K_{obs.}$	$K_{calc.}$	$\Delta \times 10^{-5}$
Ethyl alcohol	20	60	0.00126	0.00124	2
	40		0.00096	0.00097	-1
	60		0.00071	0.000735	-2.5
	80		0.00051	0.00052	-1
Methyl alcohol	20	50	0.00125	0.00124	1
	40		0.00099	0.00101	-2
	60		0.00077	0.000805	-3.5
	80		0.00060	0.00063	-3
Glycerol	20	80	0.00141	0.00140	1
	40		0.00118	0.00119	-1
	60		0.00096	0.00101	-5
	80		0.00079	0.00085	-6

$\Delta = K_{obs.} - K_{calc.}$

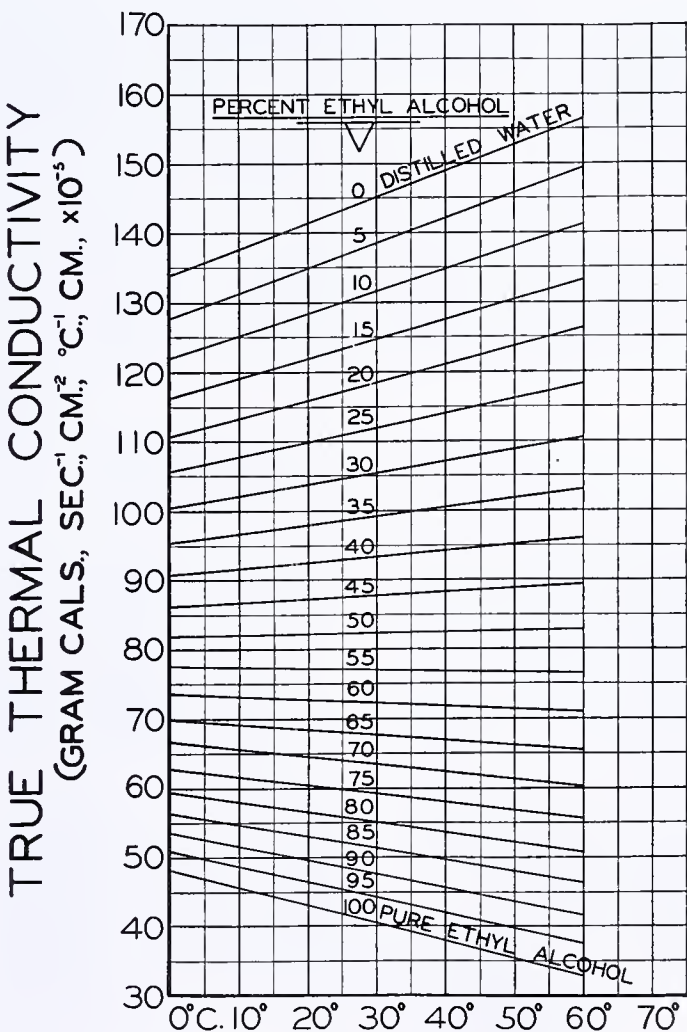


FIGURE 5. THERMAL CONDUCTIVITY-TEMPERATURE CURVES FOR ETHYL ALCOHOL-WATER SOLUTIONS



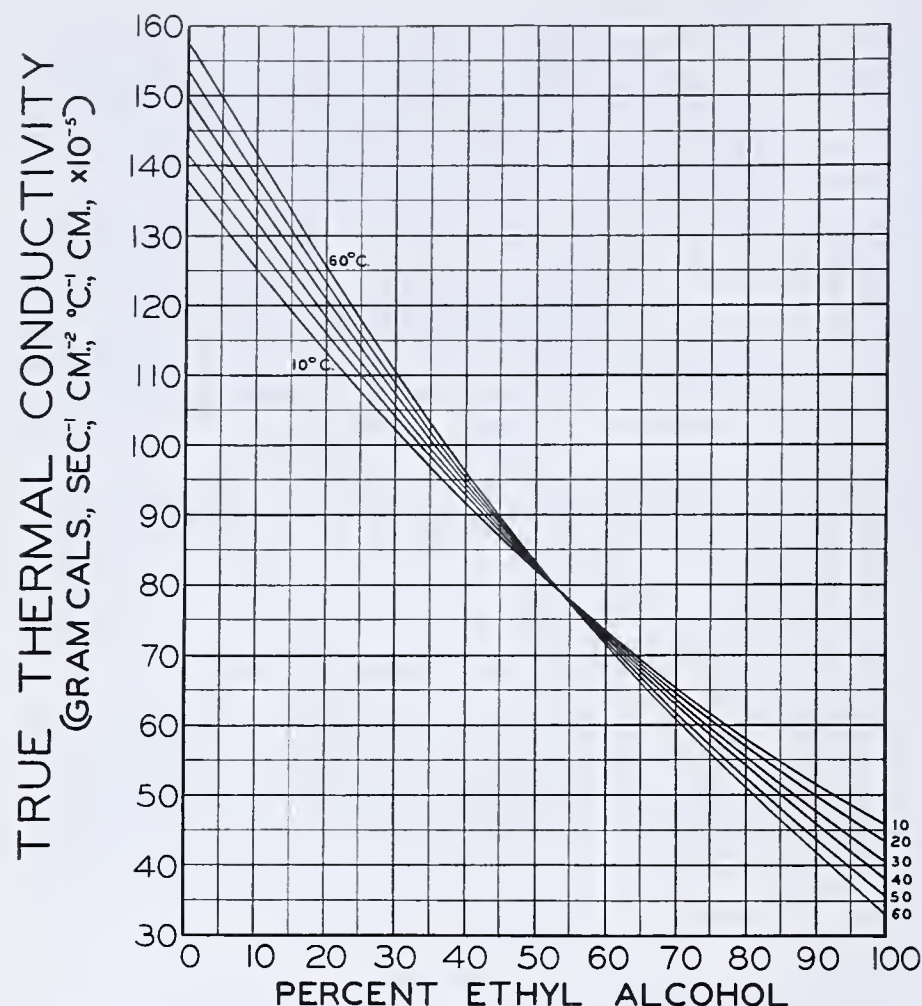


FIGURE 6. THERMAL CONDUCTIVITY-COMPOSITION CURVES FOR ETHYL ALCOHOL-WATER SOLUTIONS

versity for their coöperation in the general research program. Acknowledgment is also made to E. I. du Pont de Nemours & Co., Inc., for their permission to publish the data on the thermal conductivity of methyl alcohol-water mixtures.

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for doing so would not appreciably improve the fit of the equation.

The authors wish to express their appreciation to Laurens H. Seeyle and to Ward C. Priest of The St. Lawrence Uni-

## Determination of Gold and Silver in Cyanide Solutions

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ROUTINE control assays for the gold and silver content of the alkali cyanide leach solutions from crushed ore, and on the barren solutions after recovery of most of the precious metals therefrom, are made by many methods. The procedures most commonly employed are the copper sulfate method as used in South Africa (2), the evaporation method (2, 3), and the zinc-lead acetate method (3).

The work of Yasuda (4), and as extended by Caldwell and McLeod (1), shows that minute quantities of gold may be obtained from large volumes of solution by employing a semicolloidal mercury and mercurous chloride collector. Although their method, as reported, is not applicable to cyanide-containing solution, it was desired to apply its general principle and procedure to determining the noble metal content of cyanide-containing solutions. The problem, then, was to destroy or eliminate the cyanide ion of the samples containing noble metal so that it would not interfere with collection of gold from solution by mercurous precipitate.

A well-known inorganic reaction is the formation of potassium ferrocyanide by the reaction of ferrous sulfate and potassium cyanide. It seemed feasible with the use of ferrous sulfate to eliminate the cyanide ions from the solution that the colloidal mercury fall method should yield good results as a collector of gold and silver from solution.

To test the applicability of the semicolloidal mercury fall method in collecting and recovering gold and silver from cyanide-containing solution, if the cyanide ion is converted to ferrocyanide by use of ferrous sulfate, numerous experimental runs were made. Simulated cyanide leach solutions as from gold ores were prepared. Particles of pure gold, weighed to within 0.01 mg., were dissolved in the minimum quantity of aqua regia and transferred to water in 2-liter bottles. A measured volume of standard silver nitrate was introduced. Potassium cyanide was added to yield solutions of various percentages of cyanide, but in general of about 0.025 per cent, which is representative of economic leach solutions.



TABLE I. DETERMINATION OF GOLD AND SILVER							
Volume of Sample		Amount Used		Amount Recovered		Recovery	
Ml.	Assay tons	Au Mg.	Ag Mg.	Au Mg.	Ag Mg.	Au %	Ag %
Ferrous Sulfate-Mercurial Method							
2000	66.67	4.56	10.48	4.38	10.37	96.2	98.8
		6.80	31.44	6.39	29.21	93.9	93.0
		0.65	10.48	0.62	9.96	95.4	95.0
		1.87	20.96	1.80	20.69	96.2	98.8
		1.84	31.44	1.77	31.40	96.2	99.6
		13.85	....	13.13	....	94.8	....
		2.08	20.96	1.99	18.49	95.5	84.0
		0.52	10.48	0.49	8.17	94.3	78.0
		0.80	20.96	0.77	16.88	96.3	77.0
		0.11	11.84	0.10	9.70	90.9	82.0
		0.05	8.78	0.047	6.77	94.0	77.0
		22.93	123.00	21.36	115.00	93.2	93.5
		60.22	262.00	57.04	251.00	94.8	96.0
		0.76	22.7	0.70	18.5	92.2	81.0
		291	....	2.80	....	96.2	..
		6.65	....	6.39	....	96.0	..
		0.37	....	0.36	....	97.0	..
		1.70	....	1.60	....	94.0	..
Copper Sulfate Method							
600	20	0.90	11.52	0.86	10.99	95.6	95.4
		3.12	15.75	3.00	14.7	96.0	93.4
		12.54	62.9	12.17	59.88	96.8	95.2
Chiddey Method							
600	20	0.12	5.24	0.115	4.68	89.5	95.6
		4.96	20.96	4.79	19.46	93.0	96.5
Ferrous Sulfate-Mercurial Method							
10,000	333.3	2.08	22.21	1.95	19.68	93.0	90.0
		1.98	19.87	1.80	17.51	91.0	88.0
		0.30	...	0.27	....	90.0	..

**Method**

The method for analyzing for gold and silver from cyanide-containing solution, which has been proved applicable by analysis of simulated cyanide leach solutions of known noble metal content, and by check runs on unknowns, follows:

To 2-liter samples (about 66.67 assay tons) of cyanide-containing noble metal solution add a solution containing ferrous sulfate approximately ten times the weight of the cyanide in the sample. Add 50 cc. of a saturated mercuric chloride solution, 5 grams of magnesium powder, and 60 cc. of concentrated hydrochloric acid. Pour the acid in by portions to prevent bubbling over. If the volume of sample taken is much greater than the 66.67 assay tons (about 10 liters, 333.3 assay tons), double the amount of mercuric chloride, magnesium, and acid used. Allow to stand 6 to 8 hours, or overnight. Siphon off the clear liquid and transfer the residue from the bottle into a beaker, rinsing out any residue remaining in the bottle with small portions of water. Let it settle for a few minutes and then filter, using a rough quantitative filter paper. As the bulk of the residue is being washed onto the filter paper, sprinkle in about 20 grams of granular test lead so that the two will become intimately mixed. Allow to drain and dry.

On a bone-ash cupel weighing about 60 grams spread a layer of test lead, following the general concave shape of the cupel. Remove as much of the dried residue from the filter paper as is convenient, mash the lumps, and place in the center of the cupel. With a little lead cover the residue remaining on the filter paper, wad it up, and place on top of the cupel. Cover the residue with more test lead. The total weight of lead used should not greatly exceed 45 grams.

Introduce the cupel slowly into the muffle, so that the filter paper will be burned and mercury and its salts volatilized. This last-mentioned step must be executed cautiously and requires the close attention of the analyst; otherwise, a too rapid volatilization of the mercurial residue will cause spitting and serious losses of value, or perhaps salting of an adjacent cupellation. When a cupel has been placed in the hottest part of the muffle, increase the temperature to nearly 1000° C. and create a reducing atmosphere by putting near the cupel bits of wood, cork, or like material. When the lead has "uncovered," as shown by its bright red appearance, cool the muffle to normal cupellation temperatures. Upon completing the cupellation, weigh for gold and silver as usual in assaying. Table I lists results of analysis.

Still more accurate results may be obtained by scorification of the mercurial noble metal collection residue prior to cupellation. It is recommended that the filter paper with residue be scorified in a 6.25-cm. (2.5-inch) scorifier. Place in the bottom of the scorifier a 10-gram sheet of lead molded to the form of the scorifier. This prevents absorption of water and subsequent splattering during scorification. Add appropriate amounts of test lead and a little silica-borax glass. The scorification can be carried on so as to

yield an 18- to 30-gram button, in which case smaller sized cupels may be used.

**Discussion of Results**

A few results of analyses for gold and silver from cyanide solution by the copper sulfate method (2), and by the Chiddey or zinc-lead acetate method (3) are recorded in Table I. The percentage recovery is practically the same in the three methods. The chief advantage of the mercurial method is, then, simplicity of procedure and application to larger volumes of solution. The major loss in the various processes is probably gold and silver cupellation loss.

Analyses for gold and silver in 10 liters of cyanide-containing sample show slightly decreased noble metal recovery. In examining the results of numerous runs it was noticed that the gold recovery was between 94 and 96 per cent. If 95 per cent is considered the average of recovery, and a correction factor is applied to the weight of gold obtained, in most cases the corrected value of gold was within 0.01 mg. of the theoretical yield.

**Application of the Method**

The mercurial method is applicable to the assay of a cyanide leach solution when accuracy is desired. The corrected recovery of 0.01 mg. of gold from 66.67 assay tons of solution is estimation of the gold value to \$0.0053 per ton at the present price of gold (about \$35.00 per ounce).

The recovery of silver is subject to errors due to cupellation procedure. If, however, silver is determined within 2 mg. from 66.67 assay tons, the estimation of its value is made to within 1.5 cents per ton at the present variable market quotation of 50 cents per ounce.

The method is applicable to a pregnant cyanide leach solution, or more especially to the barren solution from which most gold and silver have been removed as a test for completeness of extraction. Merits of the method are:

But little attention is required for an individual determination.

A large volume of solution can be used conveniently, thus reducing errors in measuring and sampling.

Mercury replaces only those metals below it in the electromotive series—the noble metals. Salts of copper and other base metals in the cyanide leach solution are not reduced.

**Summary**

Gold and silver are recovered quantitatively from cyanide solutions by a semicollodial mercury-mercurous chloride precipitate in an acid medium, if the cyanide ion is first converted to ferrocyanide ion by treatment with ferrous sulfate. A determinative method for gold and silver in cyanide solutions is presented. An accuracy within 0.01 to 0.02 mg. for gold and within 2 mg. for silver is obtained from 66.67 assay tons of solution.

But slightly decreased gold and silver recovery is attainable from 333.3 assay tons of sample.

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# Photometric Determination of Vanillin in Vanilla Extracts

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ALTHOUGH the method of Folin and Denis (2) as outlined by the Association of Official Agricultural Chemists for the colorimetric determination of vanillin by means of phosphotungstic-phosphomolybdic acid reagent is in general satisfactory, it was observed that *o*-iodoxy ammonium benzoate develops a color with solutions of vanillin, suitable for photometric analysis. Because of the comparative ease of duplication of results with photometric methods, it appeared desirable to make a more detailed study of the method.

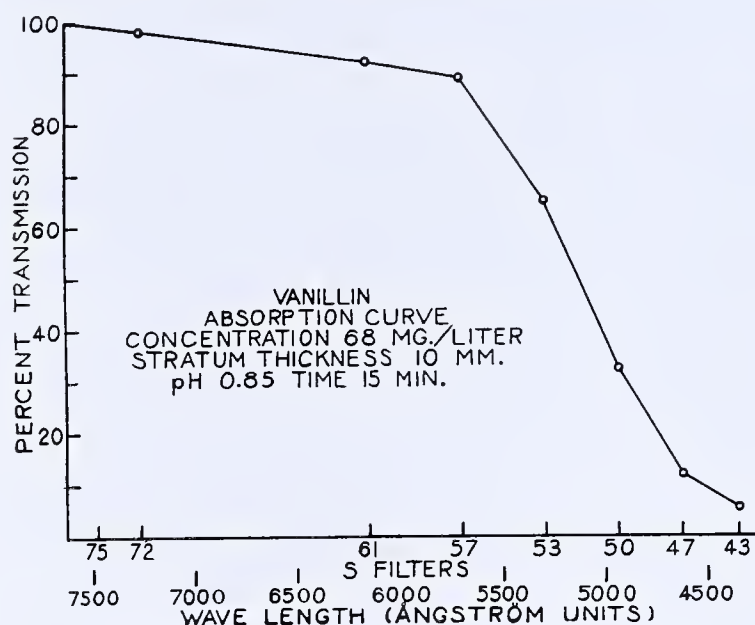


FIGURE 1

Leake (5) and his associates (Emerson, 1, and Moody, 6) have reported the use of *o*-iodoxy ammonium benzoate for the colorimetric determination of morphine and epinephrine. It was suggested by the above workers that this reagent was specific for "free phenolic hydroxyls." The authors have found that it forms color complexes with a relatively large number of types of compounds, a more detailed study of which will be reported at a later date.

Greenbaum (4) has developed a satisfactory method for the preparation of *o*-iodoxy benzoic acid and certain of its salts. The ammonium salt may be obtained under the trade name of "Amidoxyl benzoate" from the Abbott Laboratories, North Chicago, Ill.

In developing the present method it was observed that the color complex was influenced markedly by such variables as concentration of the solvent and time allowed for the development of color. A detailed study was made of the following factors in order to determine the extent of the variation: degree of absorption of the color for various segments of the spectrum, influence of hydrogen-ion concentration on the formation of the color, influence of concentration of reagent, and influence of time.

## Experimental

Figure 1 gives the light transmission of the color complex for various segments of the spectrum when the spectrum (S) filters are used. The maximum absorption occurs at the

lowest portion of the visible spectrum. Filter S43 was found to be most satisfactory for use.

By keeping the time and concentrations of vanillin and reagent constant, a study was made of the light transmission with change in hydrogen-ion concentration. It had been previously determined that a strongly acidic solution is necessary for the reaction (curve II, Figure 2). At a pH of 0.85 to 0.94, the absorption is greatest and the color is most stable.

Working at a pH of 0.87 and keeping the concentrations of vanillin and reagent constant, a study was made of the effect of time on transmission.

TABLE I. ANALYSIS OF VANILLIN SOLUTIONS

Sample	Vanillin Present G./100 cc.	Vanillin Found	
		By official colorimetric method G./100 cc.	By photometric method G./100 cc.
1	0.100	0.107	0.098
2	0.150	0.149	0.145
3	0.200	0.188	0.205
4	0.250	0.239	0.247
5	0.300	0.279	0.298

The results are shown in Figure 2 (curve I). It will be observed that it requires 15 minutes for the full development of color, following which it remains constant for several minutes. Repeated determinations show that best results are obtained by starting the readings exactly 15 minutes after the addition of the reagent, and by completing the readings during the next 5-minute interval.

REAGENTS. *o*-Iodoxy Ammonium Benzoate. Dissolve 1 gram of *o*-iodoxy ammonium benzoate in 200 cc. of distilled water.

Hydrochloric Acid. Employing constant-boiling acid, make 1 liter of 0.167 N hydrochloric acid. (See Foulk and Hollingsworth, 3, for table of concentrations of constant-boiling hydrochloric acid.)

PROCEDURE. Pipet 10 cc. of the vanilla extract into a 50-cc. volumetric flask, add 25 cc. of water and 5 cc. of 8 per cent lead

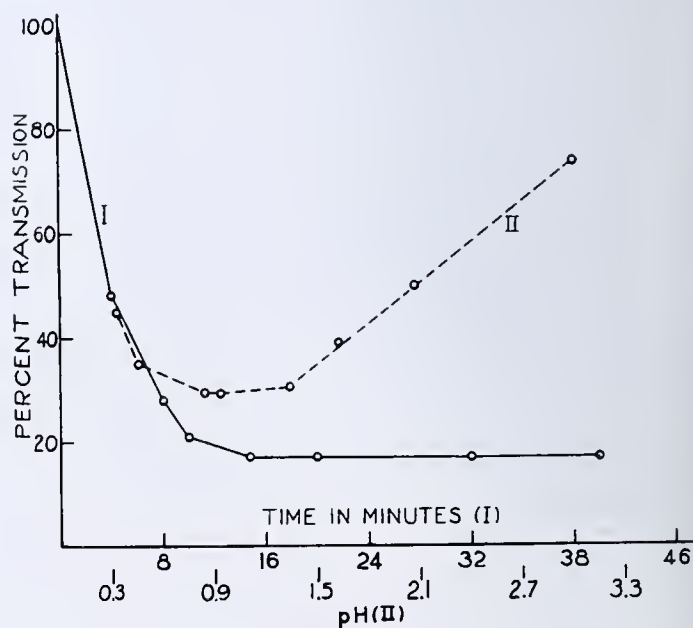


FIGURE 2



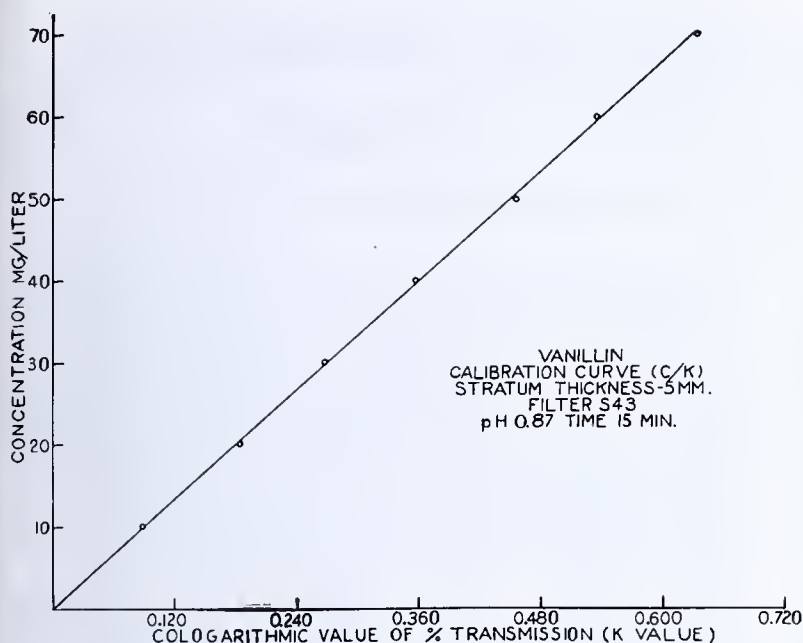


FIGURE 3

acetate solution, and make up to 50 cc. with water. Filter through a dry filter. (If a complete analysis is being conducted, 2 cc. of the clear lead filtrate as prepared for the official gravimetric determination of vanillin and coumarin may be employed.)

Pipet 5 cc. of the clear lead filtrate into a 50-cc. volumetric flask and add 25 cc. of 0.167 *N* hydrochloric acid. Shake, add 3 cc. of a 0.5 per cent solution (2 cc. are sufficient for lower concentrations) of *o*-iodoxy ammonium benzoate, and fill the flask to the mark with 0.167 *N* hydrochloric acid. Shake thoroughly and allow the mixture to stand for exactly 15 minutes. In the meantime prepare in the same manner a reference solution, omitting the reagent. Transfer to 5-mm. photometer cells and read the per cent of transmission on spectrum filter S43. Filtration of the color complex is not necessary.

By referring to the concentration curve (Figure 3), the concentration of vanillin may be read off directly from the *K* value (cologarithm of per cent transmission) in milligrams per liter. This value must be multiplied by 5.0 to convert it to milligrams in 100 cc. of the original extract. The straight-line graph shows that Beer's law holds within these limits. The concentration curve was prepared from known concentrations of vanillin (Monsanto).

Table I shows the results of analysis of vanillin solutions of known strength by both the official colorimetric method and the above photometric method.

Determinations were made on two samples of commercial vanilla extracts in order to compare the method with the standard gravimetric procedure. The extractions were made in triplicate and the average of the three determinations was taken (Table II).

TABLE II. ANALYSIS OF VANILLA EXTRACTS

Sample	Gravimetric Method G./100 cc.	Photometric Method G./100 cc.
1	0.360	0.365
2	0.086	0.082

Sample 1 was an imitation vanilla extract, colored artificially. Upon extraction and evaporation of the solvent it gave residues that were almost free from color. Sample 2 was a commercial tincture of vanilla, N. F. V. The residues obtained on extraction contained an appreciable amount of color and probably should have been further purified.

### Use of the Cenco-Sanford-Sheard Photometer

The Cenco-Sanford-Sheard photometer may also be employed for the above method by using a 10-mm. cell and a

Corning filter (H. R. lantern blue 554, 5.10-mm. thickness). A satisfactory concentration curve (Figure 4) is obtained by employing 5 cc. of the lead filtrate from the vanilla extract and only 2 cc. of the *o*-iodoxy ammonium benzoate solution. By plotting transmission against concentration on semilogarithmic paper *w/v* per cent of vanillin may be read directly from the graph. Because of the filter characteristics it is essential, in using this method, to make the readings exactly 15 minutes after the addition of the reagent. Concentrations from 0.05 to 0.25 per cent give most satisfactory results. Suitable quantities of the lead filtrate from the vanilla extract should be employed to give vanillin concentrations in this range.

### Summary

*o*-Iodoxy ammonium benzoate has been used in the quantitative determination of vanillin in vanilla extracts. The method is suitable for use with the Pulfrich photometer and with the Cenco-Sanford-Sheard photometer. In concentrations of 10 to 70 mg. per liter, the color complex gives a concentration curve with the Pulfrich photometer that closely approximates Beer's law. In this range determinations may be made with an accuracy of 2 to 3 per cent. Coumarin and other constituents normally remaining in the lead filtrate from vanilla extracts do not interfere. The method has been used for the past 2 years in a student laboratory and is more accurate and convenient than the accepted colorimetric procedure.

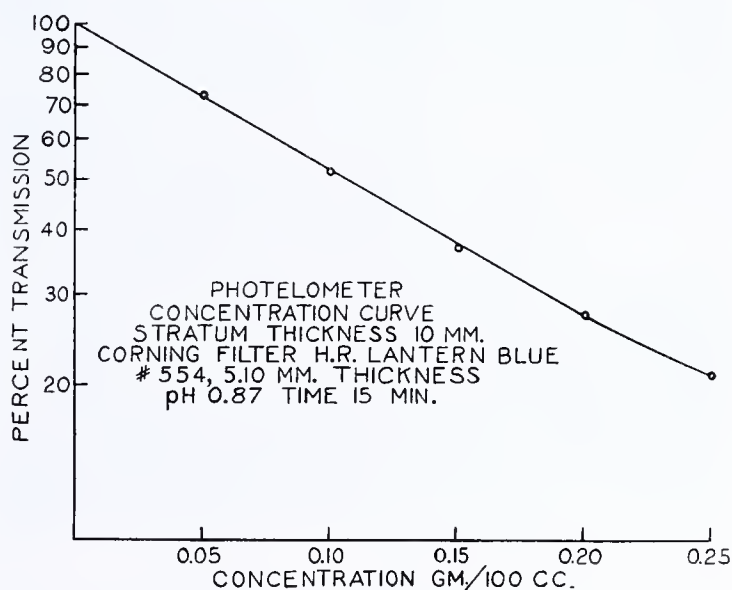


FIGURE 4

The authors wish to acknowledge with thanks the coöperation of C. D. Leake for the loan and use of the Cenco-Sanford-Sheard photometer and C. B. Gentle of the Redman Scientific Company for the loan of a Corning glass filter and general assistance with the photometer.

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# Precipitation of Calcium in the Presence of Ammonium Molybdate and Iron

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OF LATE much interest has been aroused in the determination of the calcium and phosphorus ratio in nutrition work. According to a method presented at a meeting of the Association of Official Agricultural Chemists (2) one must weigh out two charges, one for calcium and one for phosphorus. The calcium is precipitated as the oxalate by 2.5 per cent oxalic acid and 3 per cent ammonium oxalate and digested, sodium acetate is added, and the precipitate is allowed to stand 4 hours and is titrated in the usual way. The phosphorus is determined by titrating as the molybdate. Another method for calcium and phosphorus has been published by Washburn and Shear (3), who make the solution acid with hydrochloric acid, add oxalic acid, heat, add ammonium hydroxide, digest, cool, filter, and weigh. Phosphorus is determined on the filtrate from the calcium determination.

TABLE I. DETERMINATION OF CALCIUM

Sample	A. O. A. C. Method <sup>a</sup> %	Proposed Method %	Sample	A. O. A. C. Method <sup>a</sup> %	Proposed Method %
1 Skim milk, grain, bone		1.48 1.48 1.50 1.50 1.52 1.47 1.51	4 Soybean meal		0.30 0.35 0.32 0.31 0.34 0.32
2 Miscellaneous grains and meat meal	0.13	0.139 0.139 0.139	5 Dried skim milk	1.21	1.26 1.27 1.27
3 Fish meal	7.34	7.15 7.42 7.42 7.32 7.33	6 Meat scrap	10.34	10.25 10.41 10.31 10.15 10.38

<sup>a</sup> In University of Maryland Feed Control Laboratory, R. E. Baumgardner, chemist.

The following procedure, worked out here, has been successful for the determination of calcium and phosphorus. The phosphorus is first removed by precipitation as ammonium phosphomolybdate and the calcium is determined in the filtrate. By this procedure the calcium is precipitated quantitatively in the presence of ammonium molybdate and iron, under certain conditions.

## Procedure for Phosphorus

Weigh out a charge of exactly 5 grams of the finely ground sample in an evaporating dish and add about 0.5 gram of sodium carbonate. Heat the dish slowly, then at a dull red heat until a carbon-free ash is obtained. Then add 30 cc. of concentrated nitric acid and 5 cc. of concentrated hydrochloric acid, and heat the dish over a water bath to dissolve all soluble matter.

Transfer carefully to a 250-cc. volumetric flask and make up to volume. The remaining part of the procedure is the same as in the A. O. A. C. volumetric method (1). A considerable excess of molybdate is used in all cases. The filtrate and washings from the phosphorus determination are used for the determination of calcium. Calcium and phosphorus may thus be determined on the same sample with one weighing.

## Procedure for Calcium

Make the filtrate from the phosphorus, about 250 cc., slightly alkaline with ammonium hydroxide, using a piece of litmus paper in the solution as an indicator. Then acidify the solution with acetic acid added a few drops at a time, the litmus paper again serving as an indicator. Concentrated acetic acid may be used and an excess of 2 or 3 cc. does no harm. A precipitate at this point should be disregarded, so long as the litmus paper shows

that the solution is acid. Add an excess of ammonium oxalate in a solution with constant stirring, and boil the solution containing the precipitate until the precipitated calcium oxalate settles readily. Allow to stand overnight. Filter the calcium oxalate and wash free of soluble oxalates with water. Remove the filter paper from the funnel, hold it over a beaker, and wash the calcium oxalate into the beaker with a stream of water. Replace the filter in the funnel and dissolve the remaining calcium oxalate into the beaker with alternate washings of dilute sulfuric acid and hot water. Titrate in the usual way with standard permanganate.

Table I shows results obtained on samples containing varying percentages of phosphorus and calcium.

To ascertain whether this method of analysis is reliable in the presence of iron, 5 cc. of 0.1 *N* ferrous ammonium sulfate were added to the acid solution of sample 1 containing calcium and phosphorus. The solution was then boiled. The remaining part of the procedure is the same as above. The iron had no appreciable effect on the calcium determination.

Table II gives the results in the presence of the amount of iron indicated above.

TABLE II. CALCIUM IN PRESENCE OF IRON

In Solution %	Found %
1.51	1.48 1.47 1.48 1.48 Av. 1.48

As a further check upon the accuracy of the method, samples were made up as shown below. The phosphorus was precipitated according to the A. O. A. C. volumetric method (1), beginning at the point where the solution is made just alkaline with ammonium hydroxide. The calcium was determined on the filtrate from the phosphorus determination according to the method herein described.

**SOLUTION USED.** 0.1 *N* calcium nitrate, prepared by dissolving chemically pure calcium carbonate in nitric acid. This solution was checked carefully as to calcium content.

0.1 *N* iron solution prepared from ferrous ammonium sulfate and oxidized with nitric acid. This solution contained 1.861 grams of iron per liter.

0.1 *N* acid sodium ammonium phosphate solution, 6.97 grams per liter.

Ammonium molybdate solutions, A. O. A. C. volumetric method (1).

Table III shows results obtained in determining calcium in the presence of ammonium molybdate and ammonium molybdate and iron. Suitable blanks were run on all reagents.

## Discussion

The precipitate which is thrown down in the filtrate from the phosphorus determination by the ammonium hydroxide may not be completely dissolved when the solution is acidified with acetic acid, but will disappear when the sample is heated after adding ammonium oxalate.

No iron is precipitated while the solution is boiled after the addition of ammonium oxalate, probably because the oxalate of iron formed is slightly ionized.

When the sample contains considerable iron, the solution above the precipitated calcium oxalate will be decidedly greenish in color.

The calcium oxalate precipitated from samples high in iron has the same appearance as that from samples in which no iron is present. It was not, however, tested for iron.



The solution in which the calcium was precipitated had a volume of about 250 cc., and contained from 0.25 to about 2 grams of molybdic oxide in the form of ammonium molybdate. There was no visible evidence of the reduction of the molybdate by the ammonium oxalate. When considerable amounts of magnesium are present, double precipitation of the calcium oxalate would no doubt be necessary.

TABLE III. CALCIUM IN PRESENCE OF AMMONIUM MOLYBDATE AND IRON

Sam- ple	0.1 N Calcium Nitrate Added Cc.	0.1 N Acid Sodium Ammonium Phosphate Added Cc.	0.1 N Iron Solution Added Cc.	Ammonium Molybdate Added (about 5% MoO <sub>3</sub> ) Cc.	Calcium Present Gram	Calcium Found Gram
1	10.00	25.00	0.00	25.00	0.0200	0.0201
2	10.00	25.00	0.00	25.00	0.0200	0.0201
3	20.00	10.00	0.00	15.00	0.0400	0.0402
4	20.00	20.00	0.00	25.00	0.0400	0.0400
5	25.00	25.00	0.00	30.00	0.0500	0.0501
6	25.00	25.00	25.00	30.00	0.0500	0.0504
7	25.00	10.00	10.00	20.00	0.0500	0.0503
8	25.00	10.00	25.00	20.00	0.0500	0.0501
9	50.00	10.00	10.00	20.00	0.1000	0.1005

Acetic acid and ammonium oxalate dissolve the precipitate produced by adding ammonium hydroxide and ammonium molybdate to a solution containing the aluminum ion. To bring about this solution, heating is necessary. It would be

interesting to know if calcium could be quantitatively precipitated by the foregoing method in the presence of a considerable quantity of aluminum. The amount of calcium found and of calcium present agreed within the limits of analytical error.

Summary

Both calcium and phosphorus are determined on the same charge. Calcium may be accurately determined by precipitating it as the oxalate and titrating with potassium permanganate after removing the phosphorus as ammonium phosphomolybdate. Moderate amounts of iron do not interfere. It is evident that ammonium molybdate does not interfere with the quantitative precipitation of calcium in the presence of a moderate amount of acetic acid and ammonium oxalate.

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# Transposition of Silver Thiocyanate by Sodium Chloride

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IN 1916 Curtman and Harris (1) pointed out that when a mixture of silver thiocyanate and silver iodide is treated with a 5 per cent solution of sodium chloride and the mixture is boiled for several minutes, only the silver thiocyanate is transposed. The difference in the behavior of the silver salts under these conditions was made the basis for a qualitative method for rapidly detecting thiocyanate in the presence of iodide. In this investigation, the purpose was to determine the optimum conditions for effecting a maximum transposition of silver thiocyanate by sodium chloride solution, and to ascertain whether or not the test of Curtman and Harris was capable of affording quantitative indications.

Experimental

PREPARATION OF SILVER THIOCYANATE. To 10 ml. of 0.25 N silver nitrate solution were added 3 ml. of concentrated nitric acid. The whole was diluted to about 50 ml. and heated to boiling, and with constant stirring exactly the desired amount of potassium thiocyanate was added dropwise. The mixture was then allowed to boil gently to coagulate the precipitate. After standing for a short time, the precipitate was transferred completely to a filter, and washed free from silver. TRANSPOSITION OF SILVER SALT. The precipitate and paper were transferred to a beaker and treated with a definite volume of M sodium chloride solution. The mixture was boiled for the requisite time, and then filtered as rapidly as possible. The precipitate and paper were washed free from thiocyanate, and the combined filtrate and washings were collected. (Throughout this investigation M sodium chloride was used instead of the 5 per cent solution used in the original investigation of Curtman and Harris, the former being practically equivalent to the latter.) QUANTITATIVE DETERMINATION OF THIOCYANATE. The thiocyanate in the filtrate and washings was determined by precipitating it as cuprous thiocyanate, dissolving the latter in nitric

acid, and determining the copper iodometrically in the usual manner. CONTROL. The sodium thiosulfate was standardized against the potassium thiocyanate solution as follows: To 10.00 ml. of potassium thiocyanate solution (equivalent to about 100 mg. of thiocyanate ion) 60 ml. of M sodium chloride were added, and the thiocyanate was determined as above described. (Duplicate determinations were made by boiling the thiocyanate and sodium chloride for 5 minutes to determine whether there was any loss due to decomposition or boiling. None was discovered.) The per cent of transposition was then calculated as follows:

Per cent transposition =  $\frac{\text{Na}_2\text{S}_2\text{O}_3 \text{ determined}}{\text{Na}_2\text{S}_2\text{O}_3 \text{ control}} \times 100$

The results of numerous determinations of the per cent of transposition are given in Table I.

TABLE I. TRANSPOSITION DETERMINATIONS

AgCNS in Terms of CNS - Mg.	Volume of NaCl Ml.	Time of Boiling Min.	Transposition %	Mg.
Series A				
100	60	2	81.2	..
100	60	3	91.6	..
100	60	5	94.3	..
100	60	10	94.4	..
Series B				
100	25	5	51.9	..
100	40	5	91.1	..
100	60	5	94.3	..
100	80	5	94.8	..
100	100	5	97.5	..
Series C				
30	60	5	96.5	28.9
50	60	5	96.5	48.2
100	60	5	94.3	94.3
150	60	5	61.2	91.9



### Discussion

In Series A the time of boiling was varied while the other factors were kept constant. The results indicate that the transposition is reasonably complete after 5 minutes, and that further boiling increases the transposition but slightly. Series B was run in order to discover the optimum volume of sodium chloride. The results of this series are plotted in Figure 1. The curve is seen to level off at about 60 ml. Accordingly, a volume of 60 ml. was chosen as the standard in this work. Series C shows the effect of using varying amounts of silver thiocyanate. Up to a certain point all of the silver thiocyanate is transposed but, after this point has been reached, the per cent of transposition drops, while the amount transposed remains practically constant. We must conclude, therefore, that the sodium chloride solution becomes saturated with respect to  $\text{CNS}^-$ . Therefore, the larger the quantity of silver thiocyanate, the larger must be the volume of chloride solution required to transpose it.

The foregoing conclusion is in harmony with the mass action law. The amount of silver thiocyanate transposed is governed by the solubility products of silver chloride and silver thiocyanate taken simultaneously:

$$\begin{aligned} C_{\text{Ag}^+} \times C_{\text{CNS}^-} &= S_1 \\ C_{\text{Ag}^+} \times C_{\text{Cl}^-} &= S_2 \\ C_{\text{CNS}^-} &= S_1/S_2 \times C_{\text{Cl}^-} \end{aligned}$$

From the solubility products of silver thiocyanate and silver chloride, calculated from their solubilities (2), the number of milligrams of  $\text{CNS}^-$  in 60 ml. was obtained. The values are: 36 mg. at 25° C. and 245 mg. at 100° C. The experimental value is 94 mg. of  $\text{CNS}^-$ , the temperature being well above room temperature but certainly falling below 100° C. during the process of filtering off the silver chloride and untransposed silver thiocyanate.

### Summary

The most satisfactory conditions for the transposition of silver thiocyanate by  $M$  sodium chloride are: For every 100 mg. of thiocyanate as silver thiocyanate, 60 ml. of  $M$  sodium

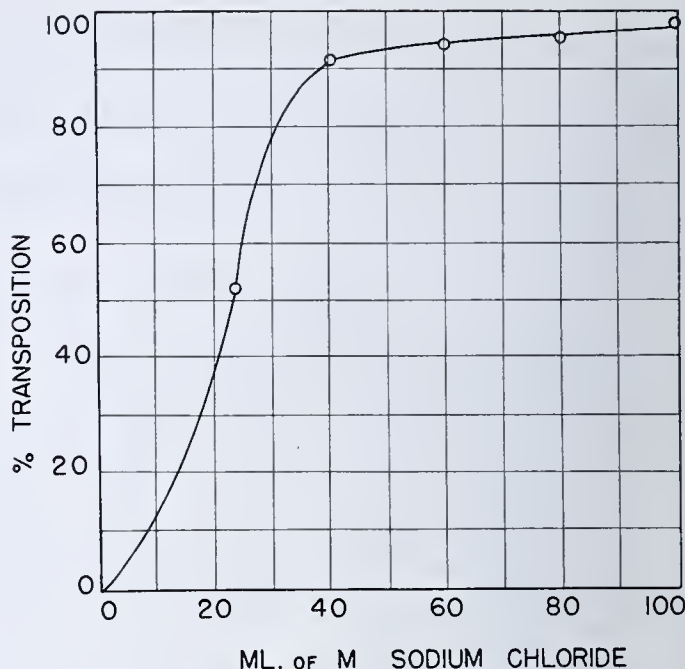


FIGURE 1. PER CENT TRANSMISSION PLOTTED AGAINST MILLILITERS OF  $M$  NaCl

chloride solution are required, and the mixture must be boiled for at least 5 minutes.

Under the above conditions a transposition of about 95 per cent of the thiocyanate is obtained.

### Acknowledgment

The authors wish to thank L. J. Curtman for suggesting this topic for investigation, as well as for his valuable advice throughout the work.

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- (2) Seidell, "Solubilities," 2nd ed., New York, D. Van Nostrand Co., 1919.

RECEIVED January 15, 1938.

## Automatic Cooling Device for Thyatron-Controlled Thermostats

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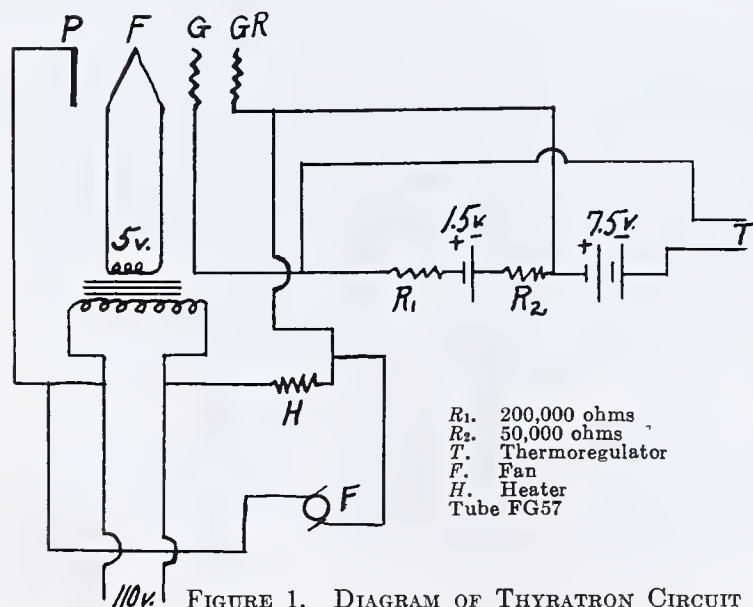


FIGURE 1. DIAGRAM OF THYATRON CIRCUIT

THE thyatron control unit, which is often used to replace the relay control unit for thermostats, is adaptable for automatic cooling as well as heating by the principle employed in a relay circuit described in an earlier paper (1).

The terminals of the fan circuit are connected in the heater circuit in such a manner that the fan and heater form a parallel circuit with the thyatron and heater. When the current is flowing through the tube the fan is shunted out of the circuit because of the high resistance of the fan motor. When no current is flowing through the tube the current will flow through the fan-heater circuit, causing the fan to run and giving only a very small dissipation of energy from the heater.

Figure 1 shows the conventional thyatron circuit with this adaptation.

### Literature Cited

- (1) Garrett, A. B., *IND. ENG. CHEM.*, **25**, 355 (1933).

RECEIVED April 29, 1938.



# Preparing Samples of Canned Dog Food for Proximate Chemical Analysis

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DURING the course of routine chemical analysis of commercial canned dog foods, difficulty was encountered in obtaining representative samples of the food for proximate chemical analysis. Since there is no official method for the analysis of canned dog foods, an attempt was made to apply to these foods the official method of the Association of Official Agricultural Chemists (1) for the analysis of canned meat products. This was found to be impossible, however, since the official method of sampling canned meats calls for initial grinding of the contents of the can in a food chopper. Pieces of intestine, green bone, and cartilage which are present in many dog foods will not pass through a food chopper or will pass through unground; furthermore, separated layers of oil in the cans are lost in the grinding process or are not thoroughly incorporated into the bulk of the food. If a small sample of the food prepared in this manner is used for analysis, a serious error due to inaccurate sampling may result. It is obvious, therefore, that the existing official methods of analysis of the A. O. A. C. cannot be applied to canned dog foods, and that a new method must be devised.

If the food is dried first, no difficulty is encountered in grinding and the material may be thoroughly mixed so that small samples may be used for analysis. The salient features of the method proposed in this paper are the initial, thorough mixing of the fresh food, the use of large samples for the determination of moisture, and the subsequent use of these dried samples for the determination of ash, ether extract, crude protein, and crude fiber. Results of moisture determinations made by the method herein described and of other proximate analyses made on the composite samples are presented to show the duplicability of results.

## Procedure

The contents of four cans of the dog food to be analyzed were emptied into the bowl of a small Hobart mixer by cleanly cutting the lid off the can, punching a hole in the bottom, and shaking the contents out in one piece. The cans were inverted and the separated oil was allowed to drain into the bowl. Any fat or oil adhering to the sides of the can was wiped out with a piece of the solid food on the end of a spatula. The food was beaten in the mixer at slow speed of the wire beater until the mass was broken up, and then at high speed for 2 minutes. The material adhering

to the sides of the bowl was pushed to the bottom with a spatula and the beater was again run at high speed for 2 minutes. The oil was thus emulsified and the larger particles were evenly distributed throughout the mass.

Three samples of this material (approximately 100 grams each) were spread evenly in thin layers on the bottom of previously tared flat-bottomed evaporating dishes 139 mm. in diameter and 32 mm. deep. The weight was determined as rapidly as possible on a heavy-duty laboratory balance with a sensitivity of 10 mg. The samples were dried at  $102^{\circ} \pm 0.5^{\circ} \text{C.}$  in an electric air oven to constant weight (12 to 24 hours), allowed to cool in a desiccator, and rapidly weighed, and the percentage of moisture was calculated from these weights. The samples were combined, ground to pass through a 40-mesh sieve, thoroughly mixed, and dried at  $102^{\circ} \text{C.}$  for 3 hours to remove the moisture taken up from the air during the grinding. The material was cooled in a desiccator and stored in tightly stoppered bottles. All subsequent proximate analyses were made on these composite samples.

In some dog foods, the presence of large amounts of fat prevented the passage of the material through the sieve, no matter how finely it was ground. Thus it was difficult to ascertain whether or not the sample was finely enough ground to be used for crude-fiber and ether-extract determinations. In this case a small portion of the ground food was extracted with ether and sifted; if it still did not pass through the 40-mesh sieve, the original sample was reground as finely as possible.

The results of moisture determinations made on 23 brands of commercial canned dog food by this method are given in Table I, as well as results of other proximate analyses made on the composite samples by the official methods of the A. O. A. C. (1).

## Discussion

The homogeneity of the samples of canned dog food prepared by this method is demonstrated by the excellent agreement between samples in Table I. These analyses, with the exception of the moisture determinations, were made on the composite dry sample and the percentage composition was calculated on the fresh basis from the average moisture content of the three individual samples.

Since canned dog food, when spread in thin layers, dries to a very porous mass, the residual moisture content may be con-

TABLE I. ANALYSIS OF COMMERCIAL CANNED DOG FOODS

Brand Number	Moisture		Sample 3	Ash		Crude Protein		Crude Fat		Crude Fiber	
	Sample 1	Sample 2		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
	%	%	%	%	%	%	%	%	%	%	%
1	46.27	46.30	46.43	1.70	1.70	13.82	13.98	25.39	25.42	0.85	0.86
2	66.25	66.37	66.42	4.20	4.20	13.41	13.46	3.86	3.87	1.31	1.38
3	68.07	68.20	68.28	3.83	3.83	8.45	8.51	4.49	4.66	0.84	0.87
4	69.88	69.89	69.93	5.15	5.15	9.61	9.65	3.51	3.53	0.77	0.79
5	70.04	70.07	70.30	4.79	4.80	8.85	8.93	1.66	1.68	1.12	1.13
6	70.06	70.20	70.48	2.80	2.82	11.31	11.39	4.76	4.87	0.68	0.71
7	70.50	70.50	70.57	2.79	2.81	10.18	10.19	2.74	2.74	0.84	0.86
8	71.10	71.28	71.79	2.22	2.27	9.11	9.13	4.83	4.84	0.67	0.68
9	71.15	71.18	71.22	3.77	3.82	7.31	7.41	2.28	2.32	1.33	1.38
10	71.33	71.46	71.48	1.40	1.42	10.40	10.44	6.12	6.13	1.62	1.65
11	71.56	71.57	71.67	1.76	1.77	12.16	12.28	3.68	3.68	0.79	0.80
12	71.84	71.91	71.91	0.85	0.85	8.36	8.42	3.24	3.24	0.51	0.54
13	72.48	72.52	72.88	1.09	1.11	11.41	11.48	3.79	3.79	0.88	0.88
14	73.04	73.22	73.48	2.48	2.49	10.77	10.79	3.34	3.48	0.77	0.84
15	73.26	73.45	73.73	2.78	2.81	7.09	7.19	2.00	2.07	0.84	0.88
16	73.88	73.89	74.02	3.31	3.31	10.70	10.73	2.40	2.40	0.93	0.94
17	74.81	75.06	75.21	2.65	2.66	6.20	6.24	1.85	1.85	0.88	0.88
18	75.71	75.72	75.86	3.21	3.21	9.16	9.18	2.15	2.15	0.78	0.80
19	76.39	76.66	76.71	1.80	1.80	9.44	9.47	0.45	0.46	1.19	1.24
20	76.30	76.81	76.86	2.26	2.27	5.61	5.65	1.24	1.25	0.98	0.99
21	76.95	76.99	77.18	0.90	0.91	6.56	6.94	0.80	0.81	2.12	2.24
22	77.46	77.53	77.57	0.96	0.96	7.30	7.48	1.55	1.56	1.10	1.19
23	79.48	79.49	79.69	1.35	1.36	4.65	4.67	0.80	0.82	0.84	0.85



sidered negligible in a substance containing 70 to 80 per cent moisture. Even though the fresh material is thoroughly mixed, a large sample should be used for the moisture determination in order to obtain a representative share of the larger particles. After this material has been dried, ground, and thoroughly mixed, it is homogeneous and small samples can be used safely for other analyses.

Ether-extract determinations were made on samples stored in tightly stoppered bottles at room temperature for 12 weeks. No appreciable difference was noted between these values and those obtained from the freshly prepared samples. As the other constituents may be considered stable, it appears that these samples may be stored for at least 12 weeks without appreciable change in the values obtained by proximate chemical analyses. These samples, however, are extremely hygroscopic and should not be unduly exposed to the air.

The Dog Food Division of the Institute of American Meat Packers (2) has recommended a method for the preparation of samples and determination of moisture content of canned dog food in which the food is first dried sufficiently to permit grinding and the moisture content is calculated. The food is then ground, mixed, and subsampled to determine the residual

moisture content. This method is open to the criticism that dog foods which have been dried sufficiently to grind easily are often hygroscopic enough to take up considerable amounts of moisture from the air during the grinding, rendering the subsampling inaccurate. Thus the accuracy of the method is dependent upon the humidity of the air and the moisture content of the food during the grinding process. In the method proposed in this paper, this possible source of error is eliminated by determining total moisture before the food is ground.

The use of the composite dry sample, obtained from the moisture determination for the other proximate analyses, eliminates to a great extent the errors which usually accumulate in the value obtained for nitrogen-free extract.

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- (1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 4th ed., p. 353 (1935).
- (2) Dog Food Division, Institute of American Meat Packers, "Methods of Chemical Analysis for Canned Dog Foods."

RECEIVED February 2, 1938.

## Syringe Attachment for Accurate Volumetric Work

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BY PROVIDING suitable stops for measuring linear displacement, the hypodermic syringe is capable of exceptional accuracy in volumetric measurement, thus replacing the volumetric pipet, as has been shown by Krogh and Keys (1, 2).

A modified arrangement as shown in Figure 1 has the ad-

vantage of readily eliminating any air bubbles produced during filling and is also more convenient to handle in use. It is simple in construction and may be attached to the ordinary syringe. The shape of the flange, *D*, at the top of the ordinary syringe makes it very convenient to use as a stop.

The adjustable rod, *C* (Figure 1), is threaded into a metal cap, *A*, which fits over the end of the plunger and is held in position after calibration by a lock nut. The top of the plunger and the top flange of the syringe should be ground on a flat glass plate with fine silicon carbide before assembly. Naturally this grinding should be as nearly at right angles to the axis of the syringe as possible. The cap, *A*, is held on the plunger by a threaded collar, *B*, and a suitable washer of fiber or soft metal.

In use the syringe is slowly filled until by a slight rotation the end of the rod may slip over the projecting flange. The excess liquid is then discharged. The exact volume is then ready for discharge and by a slight reverse rotation the rod slips over the side of the flange.

The syringe is excellently adapted to blood chemical analyses, where the exact volume of blood may be measured at the time of taking the sample and added directly to the tungstic acid or other precipitating fluid. In drawing blood it is almost impossible to avoid the formation of some gas bubbles or foam. By taking slightly more than the desired sample, and then inverting the syringe, the bubbles together with the excess sample can be discharged into absorbent cotton.

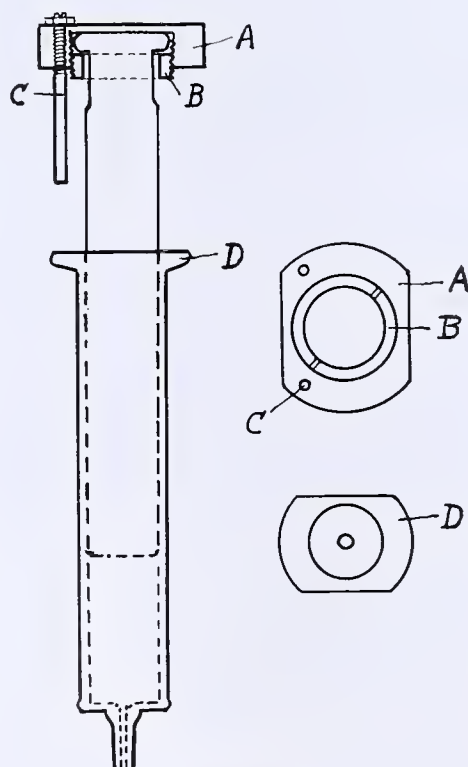


FIGURE 1

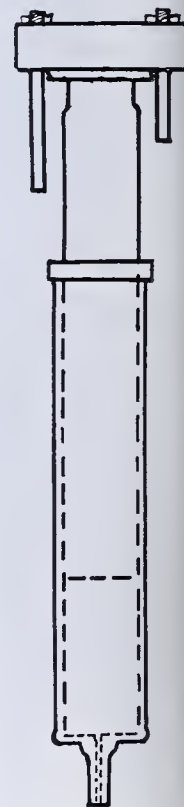


FIGURE 2



A cleaner delivery results from using a needle with the syringe, and because of the small size droplets produced accuracy is more readily obtained. A 16- or 18-gage needle gives drops small enough for ordinary work where 5-cc. samples or larger are used.

Calibration is readily made with distilled water by weighing the discharged sample and adjusting the threaded rod which may then be locked in position by the locking nut.

By providing two rods of different lengths as shown in Figure 2, the syringe may be made to deliver three different volumes, one for each rod and one for their difference in length—for example, with rods for 2 and 5 cc., a 3-cc. volume may be obtained by going from the 5-cc. position to the 2-cc. position.

Such a syringe appears to have the following advantages over a pipet, many of which have been already listed by Krogh:

1. It is much faster to use, since there is no drainage time.
2. Volatile or poisonous liquids may be handled without danger.
3. Considerably greater accuracy is attainable. Using well-constructed 10-cc. syringes, calibration is readily carried out to 1 mg. or 0.001 cc. of water. For samples smaller than 2 cc., greater accuracy can be obtained by using smaller syringes.
4. Fluids of increased viscosity or poor drainage are measured without increased error.

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- (1) Krogh, A., *IND. ENG. CHEM., Anal. Ed.*, **7**, 130 (1935).
- (2) Krogh and Keys, *J. Chem. Soc.*, **1931**, 2436.

RECEIVED January 31, 1938.

## Apparatus for Evaporating Solutions on Electrodes

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SOME methods of quantitative spectrographic analysis involve the evaporation of definite amounts of solutions directly on electrodes. Need for an apparatus by means of which several evaporations could be carried out simultaneously and conveniently by one operator developed in the author's laboratory when a number of samples of drinking waters were to be analyzed spectrographically for fluorine. The apparatus, which was built for that purpose and is described below, is useful also in other work involving the analysis of solutions by spectrographic means.

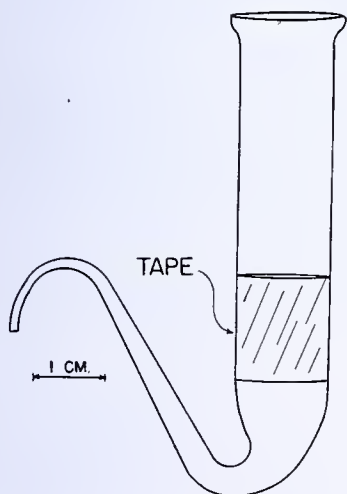


FIGURE 1. GOOSENECK PIPET

Figure 1 shows the gooseneck form of the pipets, made from 12-mm. glass tubing, that are used in the apparatus. Each pipet will hold at least 2 cc. of solution without leaking from the tip. However, the solution can be forced out at the tip by placing a finger over the large end of the pipet and pressing down. The slight piston action of the finger in the pipet then forces the solution out. A strip of adhesive tape around the body of each pipet keeps them from slipping when placed in a wooden clamp.

The arrangement of the pipets, electrodes, and other parts of the evaporator is shown in Figure 2, where twenty electrodes and a unit of twenty pipets are mounted in position for the evaporation of solutions. Twenty other pipets removed from the apparatus show more clearly the arrangement of the parts. The electrodes fit in holes in the copper bar, A, and setscrews hold the

electrodes firmly in place. A piece of heavy copper sheet, B, bent to form a flat-bottomed trough that is open at the two ends, is fastened in an inverted position on the bottom of the copper bar. The bar is about 2.8 cm. (1.125 inches) square by 37.5 cm. (15 inches) in length.

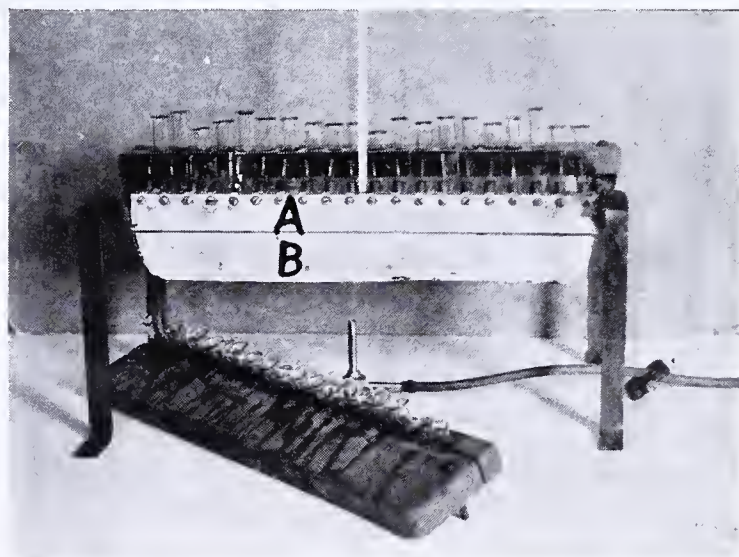


FIGURE 2. EVAPORATOR

In using the apparatus, the electrodes and pipets are put in place, then measured representative portions of the solutions to be analyzed are introduced into the gooseneck pipets. The bar is then brought to the proper temperature by regulation of the microburner, and the solutions are forced dropwise from the pipets and onto the electrodes where the evaporations take place. At the finish of the process, about 2 drops of pure solvent are placed in each pipet in order to transfer the last part of each solution to its electrode.

The rate of evaporation depends principally on the bar temperature, which is usually maintained high enough for rapid evaporation without boiling or spattering of the solutions from the electrodes.

RECEIVED February 28, 1938.



# An Automatic Continuous Percolator

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DURING the course of investigations of a number of plant materials, it was found necessary to percolate the ground plants thoroughly with a solvent such as ether or petroleum ether. Large Soxhlet extractors are rather expensive and often do not work so efficiently or smoothly as the small ones. When nearly complete extraction is desired, the usual process of percolation is laborious and time-consuming. To overcome these difficulties, an automatic percolator was constructed which is simple, compact, inexpensive, and efficient, and, when once regulated, will operate for long periods without requiring attention and with very little loss of solvent.

The apparatus is illustrated in the diagram.

The percolator, A, which holds the material to be extracted, was made by cracking off the bottom of a bottle of appropriate size and grinding down the sharp edge on a flat glass plate with a little silicon carbide powder and water. The condenser, B, is an efficient and compact distilling condenser. Tube D should be 10 mm. or more wide to permit the unobstructed passage of solvent vapor from the three-neck flask, C, to the condenser.

To operate the percolator the apparatus is assembled as shown in the diagram, a small piece of cotton being packed loosely in the bottom of the percolator so that it covers the top of tube F. The material to be extracted is then packed loosely and evenly in the percolator and covered with a few sheets of filter paper to prevent particles from floating into the overflow tube, E. The filter paper may be lightly weighted down if necessary. Solvent is poured into the percolator so that it percolates through the material to be extracted and does not run into the flask through the overflow tube. Enough solvent should be poured through the material so that the three-neck flask is about half full. The percolate runs down into the flask through tube F, which

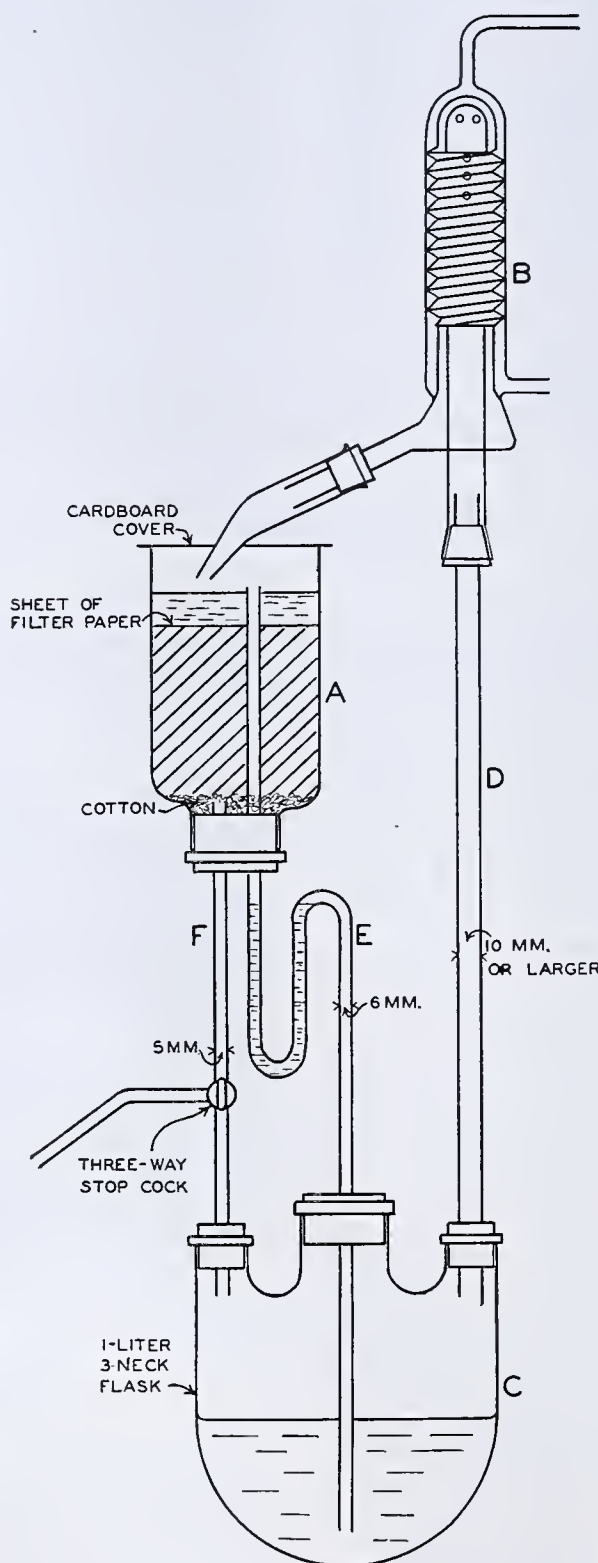
contains a stopcock and a side arm through which the percolate may be sampled at any stage of the percolation. The rate of percolation is also controlled by adjusting this stopcock. The three-neck flask is heated on a steam bath (when using ether or petroleum ether). The solvent vapors ascend tube D and are condensed in the condenser, and the fresh solvent distills into the top of the percolator through the adapter, which is inserted through a hole in the cardboard cover of the percolator. The bottom of the adapter should be kept above the level of liquid in the percolator.

In warm weather it has been found advantageous to use a compact vertical worm condenser in conjunction with the recovery condenser, B, in place of the adapter shown in the diagram. If the solvent distills into the percolator faster than it percolates through tube F into the flask, the excess will overflow into tube E and be returned to the flask. A small, very loose plug of cotton may be placed at the top of tube E to filter the returning solvent free from floating particles, but care should be taken not to obstruct the overflow of solvent.

The rate of distillation and the rate of percolation are regulated so that the solvent distills into the percolator slightly faster than the liquid runs into the flask from tube F; there should always be a slight return of solvent through the overflow tube, E. The three-neck flask and the percolator may be larger or smaller than those shown in the diagram. A 2-liter three-neck flask used in conjunction with a 3-liter percolator has also been used satisfactorily in this laboratory.

When once regulated, the percolators have been in operation for as long as 48 hours without any attention and with very little loss of solvent. Although it is possible to use rubber stoppers even with such solvents as petroleum ether, provided they fit well into the neck of the flask, it is desirable to use special stoppers that do not swell so much.

RECEIVED April 26, 1938.







## New Research Laboratory, Columbia Chemical Division of the Pittsburgh Plate Glass Company

THE continued expansion of the research activities of the Columbia Chemical Division of the Pittsburgh Plate Glass Co. made imperative an increase in space and facilities. Therefore, an addition to the laboratory, considerably larger than the original building, was erected.

The older building consisted of three floors, one floor being below the surface of the ground at the front but above ground at the rear because of the sloping surface. Four floors were desired in the new building, and in order to preserve the architectural integrity of the combined building it was necessary to place one of the new floors partially below ground. Viewed from the street, therefore, the building appears to consist of two stories. The construction is of brick, colonial in effect with its limestone trim. The reinforced concrete floors are carried on steel I-beams. All glazing is plate glass.

The main entrance leads to a foyer on the second floor partitioned in Lumite glass block. Besides clerical offices, this floor has the research director's office, the library, a smaller laboratory, and the analytical laboratory. The library and the research director's office have ceilings covered with acoustic tile to diminish extraneous sound. The floor above, divided into two large rooms, houses the inorganic and physical section, the organic section, and a smaller room for the microanalytical laboratory. The large rooms have a series of alternating laboratory tables and equipment racks.

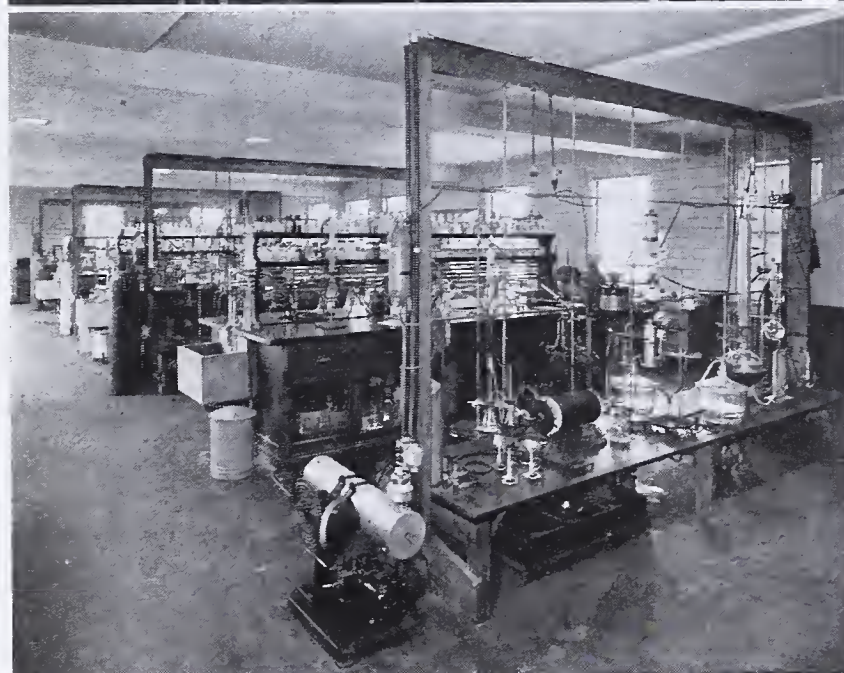
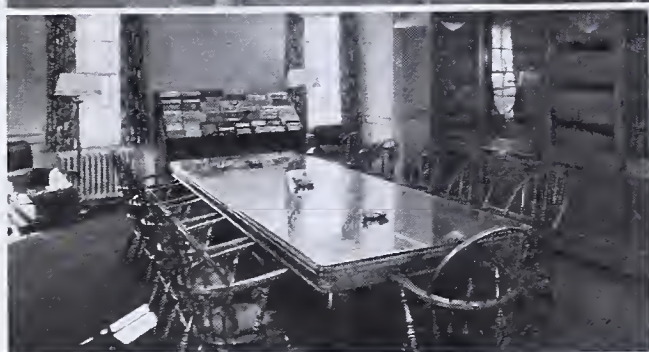
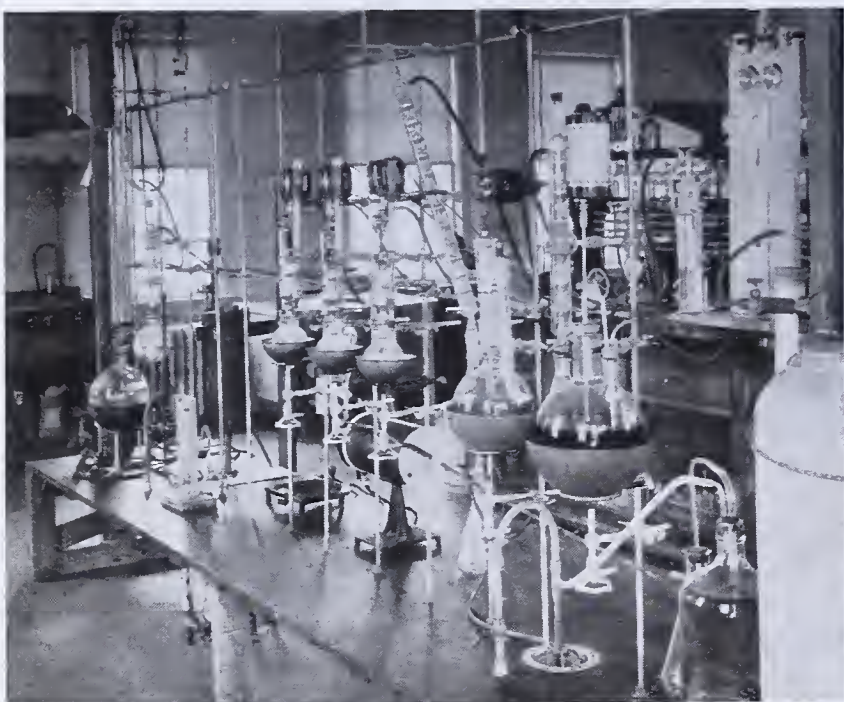
The laboratory tables are divided along the center by a waste trough, shelving, and service lines, and have Alberene stone sinks at each end. Table tops are of treated birch. Services at each table include hot and cold water, 90-pound compressed air, 110-volt alternating current, and 220-volt direct current. Except for the lead fittings at each desk, all waste lines are of Duriron for corrosion resistance. The equipment racks are provided with a stainless-steel rod system and steam lines in addition to the other services. In the new building the laboratory floors are of resilient mastic cement and office floors of asphalt tile; in the older part of the building the floors are of painted concrete with rubber mats, backed with sponge rubber in much-used places. The new building has matt-glazed ivory tile as the wall surface. Luminaries are recessed flush with the ceiling and utilize 300-watt lamps.

The microanalytical laboratory is separated from the main laboratory room by glass partitions, so that the required standards of dustlessness can be maintained. Air coming in from the outside is heated by a thermostatically controlled radiator unit and filtered through glass wool before entering the laboratory. The laboratory is of the standard Pregl type, utilizing a Kuhlmann balance and equipped for the usual microchemical determinations. The balance is mounted on a rubber ball suspension<sup>1</sup> which has proved very satis-

<sup>1</sup> Kirner, IND. ENG. CHEM., Anal. Ed., 9, 300 (1937)



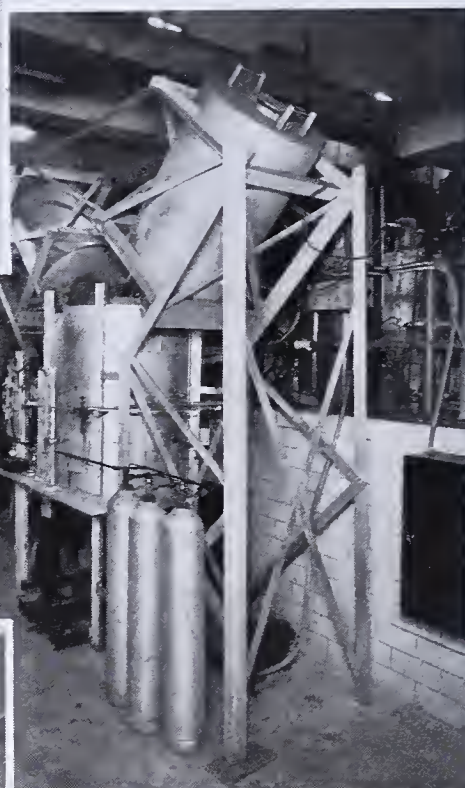




the main storeroom, with a fireproof, specially ventilated room for solvents and other inflammable material. Any increase in temperature in this room actuates controls that shut the fire door and release carbon dioxide. The technical service laboratory, equipped for rubber compounding and similar testing work, is also located here. A physical testing laboratory is equipped for pH determination (colorimetric, glass, antimony, and hydrogen electrodes) and identification by refractive index (Abbe refractometer). Other items include a light- and dark-field microscope, petrographic microscope for identification work, and photomicrographic and photo-

graphic equipment. A tool room on this floor contains a lathe, drill press, work bench, and glass-blowing table.

The basement, extending only under the newer section of the building, is devoted to pilot-plant work. Part of it has a ceiling height of 15 feet, as compared with 9 feet for the rest of the building, to accommodate larger pieces of equipment. This floor is equipped with a high-pressure (25-pound) gas line for furnacing operations, 440-volt alternating current, and 140-pound steam.



The attic of the building is used for storage purposes, but the building is so constructed that the roof may be raised and another floor added when expansion is indicated.

All floors are connected by an elevator, and much of the equipment is mounted on wheels so that it may be taken to any part of the building via the elevator without any trouble. A large centrifuge and a motor-generator set providing low-voltage high-amperage current for electrolytic work are included in the equipment of this type.

Much special equipment, such as high-pressure autoclaves and bombs designed in this laboratory, is in use.

Ventilation throughout the building is accomplished mostly through the hoods, which are of the open-face type. Fifteen to twenty air changes of the entire building an hour are exhausted through the hoods and auxiliary louvres by blowers in the attic operating through a Durimet duct system. Fresh air enters the building through louvres in the outside wall, and is passed through finned-tube heating units before entering the building.

Full use of many of the modern forms of glass are made throughout the laboratory, including, besides the uses mentioned, such things as tempered glass for special hoods and safety laminated glass shields, bound with metal edges, for surrounding hazardous operations. These shields, easily supported by laboratory clamps, are also used for the walls of thermostats housing potentially hazardous experiments.

factory. When excavations were being made for the newer building, a retaining wall, an integral part of the older building, was battered down by a 4-ton steel ball swung by a steam shovel with concussions that made the whole building tremble. It was possible, however, to carry on the micro-weighings with no noticeable aberration while the pounding was going on.

The first floor, also equipped with racks and laboratory desks, is reserved for industrial projects requiring the handling of materials on a slightly larger scale. This floor holds





# Microchemistry

## Ethanolamine in the Determination of Mercury

### In Inorganic and Organic Compounds and Pharmaceutical Preparations

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**B**ECAUSE of the increasing use of mercury compounds in medicine and other fields, the determination of mercury in its organic and inorganic salts and its organometallic compounds is becoming more and more important.

Many methods for the determination of mercury in organic compounds are recorded in the literature. In several procedures the organic compound is heated with lime or sodium carbonate and the liberated mercury is distilled onto gold foil or wire or into a gold cup, so that it may be weighed as an amalgam. Some procedures have been adapted to work on a micro scale. Other methods employ oxidative decomposition in sealed or open vessels, using such agents as nitric acid, bromine water, permanganate, dichromate, persulfates, iodine, etc. After the mercury has been converted to the ionic form it may be handled by any of the well-known methods for determining ionic mercury. Some organic compounds when treated with sodium and alcohol give up their mercury as metallic mercury, which may be estimated in various ways. In the case of some organic compounds direct electrolytic determination of the mercury is possible.

During the development of the use of monoethanolamine for the determination of halogens in organic compounds (2, 3) the observation of Meltsner, Wohlberg, and Kleiner (1) that the amine would reduce mercury salts in aqueous solution suggested its use in the quantitative determination of mercury. It has been found possible to determine mercury quickly and accurately in inorganic salts, oxides, organic salts, organic mercuric halides and nitrates, Mercurochrome, pharmaceutical ointments and tablets containing mercury compounds, and some compounds of the type  $R_2Hg$ , by the use of monoethanolamine. In some compounds containing halogen as well as mercury, the two may be determined simultaneously.

The general procedure adopted for salts, oxides, Mercurochrome, and pharmaceuticals containing such compounds consists of simply heating the solid sample with the amine for 5 minutes, whereupon the mercury is reduced to the metallic state and appears as a single globule below the liquid amine. The excess amine is quickly removed by filtration, and the globule is washed with water, transferred to a halogen filtration microtube, and weighed as such after a simple drying procedure. Alternatively, the globule of mercury is dissolved in nitric acid and titrated by means of thiocyanate.

Compounds which do not respond to the above treatment in a reasonable length of time may be handled by exactly the same method as that used for halogens (2). This procedure involves the use of monoethanolamine, sodium, and dioxane.

In some cases the substitution of diethanolamine for monoethanolamine enables the mercury to be determined without using the general halogen procedure. The apparatus has been kept very simple and inexpensive, and the procedure is simple and rapid.

Both procedures have been used successfully on micro, semimicro, and macro scales. Samples of pure compounds varying from about 3 to 370 mg. have been handled with practically no variation in technic or apparatus.

The inorganic compounds used were the best analytical grade obtainable and were dried by a suitable procedure. The organic salts were prepared from the corresponding sodium salts and were recrystallized several times from a suitable solvent. The organometallic compounds were purchased and further purified. Pharmaceutical preparations were used as purchased from drugstores.

#### Materials

The monoethanolamine,  $NH_2-CH_2-CH_2OH$ , used for the reduction of the sample was commercial material which was distilled in an all-glass outfit at atmospheric pressure. The diethanolamine,  $NH(CH_2-CH_2OH)_2$ , occasionally employed was commercial material distilled at reduced pressure in an all-glass outfit. The dioxane used as a solvent for removing the base of pharmaceutical ointments was commercial material. The dioxane used with monoethanolamine and sodium for liberating mercury bound directly to carbon was made halogen-free when halogen was to be determined in the organic compound simultaneously. For this purpose it was refluxed with monoethanolamine and sodium and then distilled (2). Acetone employed for washing and drying was dried over calcium chloride and distilled. The sodium was halogen-free.

#### Apparatus

For the reduction of the sample a  $25 \times 200$  mm. Pyrex test tube may be used with entire success. A test tube of the same dimensions but with a pear-shaped bulb at the bottom is somewhat more convenient, as the mercury globule will lie in the narrow part of the pear and thus enable the washing and filtration to be carried out more easily. A simple cold-finger reflux condenser serves to prevent loss of amine. The apparatus is thus essentially the same as that employed by the author for determining halogens on a micro scale (2). For filtration the usual Pregl micro halogen arrangement is used.

#### Method of Weighing Samples

The samples are weighed in small open weighing bottles made by cutting down specimen vials 8 to 10 mm. in diameter and polishing the cut ends. The weighing bottles are most conveniently handled by means of a pair of metal forceps, the prongs of which are bent to fit the cylindrical bottle. Solid samples are introduced into the bottles by means of a small spatula.



TABLE I. CONSECUTIVE WEIGHTS OF FILTER TUBES OBTAINED BY THE DRYING PROCEDURE

	Mg.		Mg.
	Macrobalance <sup>a</sup>		
1	5975.85	5	5975.80
2	5975.85	6	5975.90
3	5975.85	7	5875.80
4	5975.85	8	5875.85
	Microchemical Balance <sup>b</sup>		
1	5356.891		....
2	5356.895		....
3	5356.906		....
4	5356.893		....

<sup>a</sup> 5-minute aspiration, 10-minute standing at balance.<sup>b</sup> 10-minute aspiration, 15-minute standing at balance.

### Standardization of Volumetric Solutions

For standardizing the 0.02 *N* and 0.05 *N* thiocyanate solutions used for volumetrically determining the mercury in some samples, the best grade of calomel was used. A weighed sample of calomel was reduced to metallic mercury by means of monoethanolamine. The mercury was dissolved and titrated with the solution to be standardized.

All the details for the reduction and titration are given below. This method of standardization was adopted after the success of the reduction procedure had been established. As a further check on the standardization procedure, the mercury from the sample of calomel was determined gravimetrically as described below before it was dissolved for titration.

### Method I

**SALTS, OXIDES, AND MERCUROCHROME.** Slip the weighing bottle containing the sample into the digestion tube, add 3 to 5 ml. of monoethanolamine, and attach the cold finger. Suspend the digestion tube loosely from a clamp and gently boil the amine with a microburner for at least 5 minutes. In some cases colloidal mercury begins to appear as soon as the amine strikes the salt. At the boiling temperature the colloidal mercury quickly disappears and the reduction is probably complete in a very short time, but at least 5 minutes' boiling should be allowed. The mercury appears as a single globule at the bottom of the test tube or at the narrow part of the pear. Cool the tube and contents rapidly to below 100° C. by lowering the tube into a beaker of cold water, and wash down the condenser with water. After removing the condenser, add more water to bring the total volume to 15 or 20 ml. to reduce the viscosity of the amine. In some cases, but not usually, an insoluble material may appear on dilution.

When only mercury is to be determined, remove the liquid from the tube by the use of the filtration arrangement designed by Pregl for the determination of halogens, but employ a blank tube without any filtering medium. This reduces the filtration time to a matter of seconds. Correct placing of the lower end of the siphon tube facilitates removing the liquid without disturbing the mercury. Wash the globule several times with small amounts of water and suck this over as above. In each case all but a fraction of a milliliter of the wash liquid may be easily removed.

Finally bring the globule over to the prepared micro halogen filter tube by lowering the siphon over the globule and gently applying suction. If the globule breaks into several smaller globules as it falls on the mat of the filter tube, assemble these by gently tapping the tube so that the particles roll around and come into contact with each other. Wash the globule several times with water and finally several times with dry acetone. Remove the filtering tube from the suction flask and thoroughly wipe it with moist flannel. Then place it in the filtering arrangement with a perfectly dry suction flask, attach a cotton filter tube, and aspire a gentle current of air through the tube for 5 minutes. Finally place the tube near the balance and weigh it after 10 minutes. For microwork 10-minute aspiration and 15-minute standing are advisable. The filter tubes are of the type used for handling the silver halides, and have coarse sintered-glass disks and thick asbestos mats. The mats should be firmly pressed with the blunt end of a glass rod to make the upper surface as hard as possible. The tubes are prepared for use by washing with water and dry acetone and drying as indicated above.

Some years ago Willard and Boldyreff (4) tried a somewhat similar method of handling metallic mercury, but used macro-

Gooch crucibles with sintered bottoms and with no asbestos. They claimed a loss of about 1.3 mg. of mercury in the drying process, which was essentially the same as outlined above. In their case the mercury was in a finely divided form and the loss was probably due to the large surface exposed to the air as it streamed through the crucible. The small surface presented by the single globule of mercury in the author's case probably accounts for the failure to note such a loss. Fairly good results were obtained on a micro scale, where the loss of any such amount of mercury as mentioned by Willard and Boldyreff would have thrown the percentage of mercury off by as much as 25 per cent in some cases.

The fact that reproducible weights of the filtering tube can be obtained by the described method of washing and drying is demonstrated by Table I. Between the consecutive weighings, the tubes were washed and dried as previously outlined.

The mercury may be determined volumetrically if desired.

Wash the globule of mercury in the digestion tube as directed, dissolve it in a few drops of concentrated nitric acid, and add a few milliliters of water. To ensure the absence of nitrous acid and mercurous mercury, add 5 per cent potassium permanganate solution dropwise until the permanganate color persists for 5 minutes. Destroy the excess permanganate with dilute hydrogen peroxide solution. Before titration with thiocyanate add 1 to 1 nitric acid and ferric alum indicator. The mercury ion may be titrated with 0.02 *N* or 0.05 *N* thiocyanate solution, depending upon the scale of the work. On a micro scale the titration may be carried out in the digestion tube, but on a macro scale it will be necessary to transfer the mercury solution (or globule) to an Erlenmeyer flask for titration. The transfer is most readily accomplished by using the Pregl filtration arrangement. For this purpose place a two-hole rubber stopper in the Erlenmeyer with a blank filter tube and apply suction to the other hole of the stopper. Rinse the digestion tube and siphon well to bring over the last trace of mercury solution.

Other methods of estimating the mercury may be used after it has been obtained in the ionic condition.

Reactive halogen in organic or inorganic mercury compound will be present in ionic form in the filtrate obtained in the first filtering and rinsing step. For determination of the halogen, the filtrate is best caught in a 25 × 200 mm. test tube. On acidifying with nitric acid and adding silver nitrate, the halogen may be determined as directed elsewhere (2).

**PHARMACEUTICALS, OINTMENTS, AND TABLETS CONTAINING MERCURY SALTS OR OXIDES.** Because of the small mercury content fairly large samples are necessary, and hence larger weighing bottles are used. The only modification of procedure necessary is with the ointments, where the ointment base must be removed after the reduction. To get rid of the ointment base, omit the rinsing of the digestion tube and condenser with water at the end of the digestion period, and filter off the liquefied ointment base and ethanolamine while still hot. Use the same filtering arrangement as in the previous case. Dissolve the last amount of base in hot dioxane or other suitable solvent and remove it by the filtration procedure. Then handle the globule in the usual manner.

With tablets the only new problem is the removal of the filler. No modification of the procedure for salts is necessary, as the filler is easily sucked away from the globule by the rinsing procedure before the globule is transferred to the filter tube.

Table II gives typical results obtained with a variety of compounds and preparations containing mercury.

### Method II

**ORGANIC COMPOUNDS OTHER THAN SALTS.** Most mercury compounds in which mercury is directly attached to a carbon atom cannot in general be reduced to metallic mercury by



TABLE II. DETERMINATION OF MERCURY IN ORGANIC AND INORGANIC COMPOUNDS AND PHARMACEUTICAL PREPARATIONS

Compound	Sam- ple	Method	Mercury Found Mg.	%	Theory %	Compound	Sam- ple	Method	Mercury Found Mg.	%	Theory %
Mercurous chloride	10.924	I	9.297	85.11	84.98	Phenylmercuric nitrate	41.61	I-D	24.60	59.12	59.06
	9.588	I	8.163	85.14	15.02(Cl)		92.00	II	54.35	59.08	
	124.20	I	105.50	84.95			101.40	I-D	60.05	59.22	
	127.75	I	108.55	84.97		Phenylmercuric chloride	11.445	II	7.335	64.09	64.07
	194.20	I	165.05	84.99						11.34(Cl)	11.38(Cl)
	368.35	I	312.90	84.95			24.74	II	15.90	64.27	
	120.25	I	V <sup>a</sup>	14.96(Cl)						11.40(Cl)	
	131.20	I	V <sup>a</sup>	14.93(Cl)			35.26	I-D	22.62	64.15	
Mercuric chloride	112.10	I	82.80	73.82	73.88		99.05	I-D	63.45	64.06	
	139.30	I	102.85	73.84	26.12(Cl)					11.38(Cl)	
	180.15	I	V	73.91		Di- <i>p</i> -tolylmercury	35.40	II	18.19	51.38	51.42
				26.08(Cl)			39.32	II	20.20	51.37	
Mercuric oxide	40.48	I	V	92.67	92.61		12.637	II	6.514	51.54	
	203.45	I	V	92.68			139.60	II	71.80	51.43	
Mercuric iodide	121.50	I	53.52	44.05	44.14		32.72	I-D		51.37	
				55.90(I)	55.86(I)	Mercurochrome	156.85	I	41.55	26.49	26.73
	156.50	I	69.10	44.15		(H. W. D., dried)	134.60	I	35.70	26.52	
				55.83(I)			175.55	I	46.65	26.57	
Mercurous iodide	116.80	I	71.61	61.31	61.25		195.40	I	V	26.56	
				38.60(I)	38.75(I)	Ammoniated mercury	752.90	I	28.52	3.79	
	136.80	I	83.93	61.35		ointment, 5% with	933.60	I	35.40	3.79	
				38.62(I)		petrolatum base	554.45	I	20.70	3.73	
Mercuric oxalate	44.50	I	30.93	69.51	69.45		637.90	I	24.18	3.79	
	180.70	I	125.50	69.45			734.10	I	V	3.79	
Mercuric <i>p</i> -toluate	9.928	I	4.226	42.97	42.62	Calomel ointment, 5%	1342.0	I	53.68	4.00	
	20.05	I	8.55	42.64			1023.4	I	41.31	4.03	
	96.00	I	40.90	42.60				I	V <sup>b</sup>	4.02	
Mercuric benzoate	3.227	I	1.463	45.34	45.32		1131.4	I	V	3.99	
	46.23	I	20.95	45.32			1234.6	I	V	3.99	
	93.55	I	42.43	45.38		Calomel tablets	265.20	I	53.07	20.01	
Mercuric phthalate	11.185	I	6.159	55.06	55.01		291.60	I	58.11	19.93	
	50.88	I	28.00	55.03			161.10	I	31.83	19.76	
	108.70	I	59.80	55.01				I	V <sup>b</sup>	19.92	
Mercuric succinate	35.36	I	22.40	63.35	63.35		374.30	I	76.29	20.38	
	67.10	I	42.50	63.34			221.70	I	44.71	20.22	
Mercuric cyanide	115.65	I-D	V	79.36	79.41			I	V <sup>b</sup>	20.25	
	105.40	II	V	79.46			389.20	I	78.65	20.21	

<sup>a</sup> Mercury from sample used for standardization of thiocyanate. <sup>b</sup> Mercury determined volumetrically after first determining it gravimetrically.

monoethanolamine in a reasonable time, if at all. However, a number of types of organic mercury compounds may be handled successfully by using the general procedure as employed for halogens in organic compounds (2). This involves the use of sodium, monoethanolamine, and dioxane in the same type of apparatus as in Method I.

Reflux the sample with 3 to 5 ml. of monoethanolamine and 2 to 3 ml. of dioxane. For microwork add about 0.2 gram of sodium in small pieces from time to time, and for larger samples use correspondingly larger amounts of sodium. The mercury set free by the reduction amalgamates with unreacted sodium and appears at the end of a half-hour, refluxing as a small hard pellet at the bottom of the tube. After the heating period, remove the liquid contents of the tube as usual and thoroughly wash the pellet with water in the tube. Cover it with about 5 ml. of water and boil the water until the amalgam no longer evolves hydrogen, showing that all the sodium has been destroyed. This usually takes about 5 minutes. From this point on the procedure is the same as in Method I.

Halogen may be determined simultaneously as in Method I.

Merely substituting diethanolamine for the monoethanolamine of Method I and refluxing for 30 minutes will give a

quantitative reduction of some organic mercury types. Analyses done in this way are designated as I-D in Table II.

### Summary

A simple and rapid method for the determination of mercury in inorganic and organic compounds and in pharmaceutical preparations has been developed. The process has been put on both a gravimetric and volumetric basis. The halogens may be determined simultaneously. The method may be used on a qualitative basis for the detection of mercury in inorganic or organic compounds.

The author was unsuccessful in trying to apply either Method I or Method II to a sample of Merthiolate kindly supplied by Eli Lilly and Company.

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# Iodometric Microdetermination of Selenate in the Presence of Selenite

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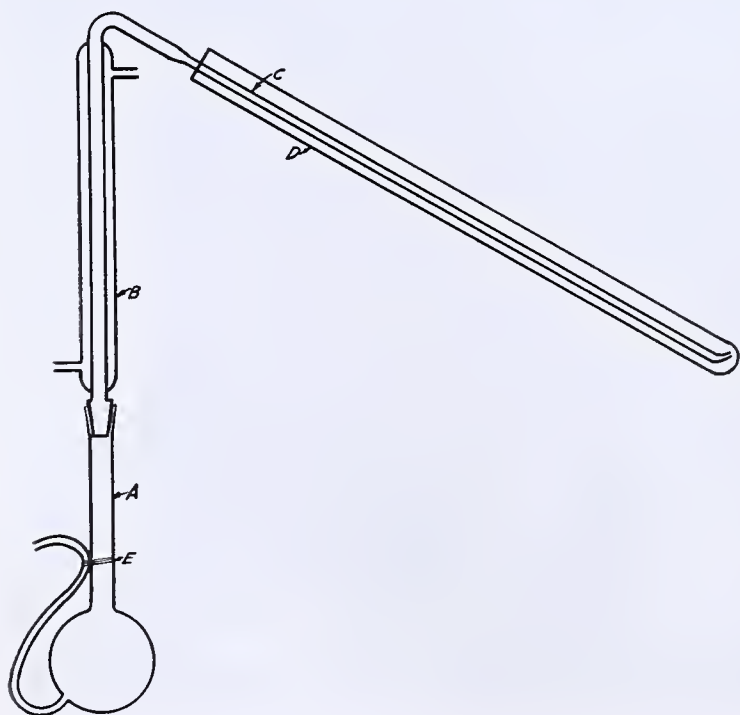
GOOCH and Evans (3) studied the conditions necessary for an iodometric method of determining selenate in the presence of selenite, based on the reaction  $\text{H}_2\text{SeO}_4 + 2\text{HCl} \rightarrow \text{H}_2\text{SeO}_3 + \text{Cl}_2 + \text{H}_2\text{O}$ , which takes place when the mixture is distilled. The chlorine evolved is absorbed in potassium iodide solution, and the liberated iodine is titrated with standard thiosulfate solution. Moser and Prinz (5), in an extensive investigation of several methods for the determination of selenium, showed that reliable results can be obtained by Gooch and Evans' procedure. In analyzing mixtures containing only a few milligrams of selenate radical in the presence of about 0.10 gram of selenite radical, the authors were not able to obtain satisfactory results by the procedure of Gooch and Evans. The experimental details of a satisfactory procedure, modified to include the use of a reflux condenser in the distilling operation, are described below. Dolique (1), who used such a modification in analyzing 0.20-gram selenate samples, states that the method is accurate to about 0.5 per cent.

## Experimental

The distilling apparatus used in this work is shown in the diagram.

The distilling flask was a 125-cc. round-bottomed flask to which a ground-glass joint of 12-mm. bore was sealed at *A*. A side tube was sealed into the bottom, as shown, to provide a convenient way of passing carbon dioxide through the apparatus. In order to prevent accidental breakage of the seal, the side tube was fastened securely at *E* with a few turns of wire. The reflux condenser tube in *B* was of 7-mm. bore and 22 cm. long, and the delivery tube, *C*, of 4-mm. bore and 50 cm. long. A tube, *D*, 17 mm. by 45 cm., was used as a container for the potassium iodide solution used to absorb the chlorine. A film of concentrated sulfuric acid served to seal the ground-glass joint. An ebullition tube 1-mm. bore was used to promote quiet boiling.

A selenic acid solution used as the selenate standard was prepared by the method described by Thomsen (6). Por-



tions of this solution when treated with hydrochloric acid and saturated with sulfur dioxide showed negative results for selenious acid. The selenate radical concentration was determined gravimetrically by reducing to free selenium with sulfurous acid according to the method of Gutbier, Metzner, and Lohmann (4). About 50 grams of sample solution were used in order to yield about 0.075 gram of selenium. The selenium obtained was weighed with a semimicrobalance, using certified weights. Duplicate analyses agreed within 0.2 per cent. In all the work given in this paper, the selenate samples were measured with a weight buret.

TABLE I. DETERMINATION OF SELENATE

Selenate Used Mg.	Selenate Found Mg.	Error	
		Mg.	%
81.78	81.74	-0.04	-0.05
76.02	76.02	±0.00	±0.00
18.62	18.60	-0.02	-0.1
18.24	18.20	-0.04	-0.2
8.24	8.27	+0.03	+0.4
2.03 <sup>a</sup>	2.02	-0.01	-0.5
1.69	1.68	-0.01	-0.6
1.06	1.07	+0.01	+0.9
1.05 <sup>b</sup>	1.04	-0.01	-0.9
1.03 <sup>b</sup>	1.05	+0.02	+1.9
0.51	0.50	-0.01	-2
0.37 <sup>c</sup>	0.36	-0.01	-3
0.27 <sup>a</sup>	0.26	-0.01	-4
0.27	0.28	+0.01	+4

Foreign substance added: <sup>a</sup> 0.10 gram  $\text{SeO}_2$ ; <sup>b</sup> 2.0 grams  $\text{Na}_2\text{SO}_4$ ; <sup>c</sup> 0.20 gram  $\text{SeO}_2$ .

Conductivity water and reagent quality chemicals were used throughout. Blanks were run to detect possible traces of iodate in the potassium iodide. Since the hydrochloric acid concentration remains essentially constant in the distillation process, it was possible to show indirectly the absence of active impurities in this reagent. This was done by adding a second sample of selenate directly to the distillation residue of the previous determination, and then proceeding as usual. No significant variations were detected in any case.

Sodium thiosulfate solution (0.01, 0.025, and 0.005 *N*) was standardized against standard potassium iodate solution. The titration end points were determined by means of the "dead stop" potentiometric method as given by Foulk and Bawden (2). The apparatus used was definitely sensitive to 0.01 cc. of 0.005 *N* iodine in a volume of 100 cc. A motor-driven stirrer was used in all titrations.

## Procedure

The receiver was filled within about 10 cm. of the top with a solution containing about 2.5 grams of potassium iodide, and placed in position. Sufficient concentrated hydrochloric acid and water were then added to the measured selenate sample in the distilling flask to give a volume of 60 cc. having 5 *N* acidity.

The carbon dioxide flow was next adjusted to a rate of about 35 cc. per minute, and the reflux condenser turned on. The solution was then heated with a microburner, and distilled for 20 minutes after the boiling point had been reached. The contents of the receiver were transferred to a 250-cc. wide-mouthed Erlenmeyer flask, followed by thorough rinsing. In order to remove any traces of iodine from the inside of the delivery tube, the carbon dioxide flow was stopped and a wet rag was momentarily touched against the side of the hot distilling flask to produce sufficient decrease of internal pressure to cause the rinse water to be drawn into the delivery tube, whereupon the carbon dioxide was again turned on to force the liquid out. In order to duplicate the acidity conditions of the thiosulfate standardiza-



tions, 2 cc. of 6 *N* hydrochloric acid were then added to the liberated iodine solution, followed by immediate titration with thiosulfate.

The results of a series of determinations are given in Table I. The quantities given are in terms of selenate radical.

### Discussion

Table I shows that reliable results were obtained over a wide range of selenate samples. Equally good results were obtained when 6 *N* instead of 5 *N* hydrochloric acid was used in the distillations. Detectable positive errors, due to the volatilization of selenium tetrachloride, were found in running blanks containing 0.10 gram of selenium dioxide in 7 *N* acid, while with 8 *N* acid positive errors corresponding to 0.4 mg. of selenate radical were found. As shown, comparatively large

amounts of sodium sulfate do not interfere. Foreign materials which are either active oxidizers or reducers under the given experimental conditions must obviously be absent, including bromide and iodide, since these further reduce the selenious acid formed to elementary selenium.

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## Determination of Zinc

### A Colorimetric Micromethod

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THE colorimetric method presented here for the determination of zinc in soil and agronomic products was developed to meet the special requirements of an investigation of the physiological effects of zinc in soil on crops growing therein, but should be applicable to the determination of zinc in many materials. Of the various methods which have been previously devised for the determination of small quantities of zinc, probably the most convenient is the turbidimetric procedure which depends upon the formation of colloidal zinc potassium ferrocyanide. This method, recently revised by Boggs and Alben (3), was found by the writer to give good results when only approximate values were required. Using a photoelectric cell to measure turbidity, the writer found that the opacity of the colloidal suspensions increased markedly with a short time of aging of the freshly prepared potassium ferrocyanide reagent. Other unexplained factors operated to cause vagaries in the results obtained. The method of Todd and Elvehjem (9), in which zinc is precipitated as zinc ammonium phosphate and calculated from a subsequent colorimetric determination of the phosphate, was found to be unsuccessful for the small quantities of zinc isolated from samples of soil. A search was made for a method that could be used to measure reliably some small differences in the zinc content of the soils and vegetation in question.

The zinc present in soil may be brought into solution by fusion with potassium pyrosulfate and separated from interfering elements by means of hydrogen sulfide as most recently employed by Boggs and Alben (3). This procedure was adopted in the present work. The zinc in plant materials may be brought into solution by ashing at 450° to 500° C. and extracting the ash with hydrochloric acid as in the procedure used by Hibbard (4), or the ash may be fused with potassium pyrosulfate to render the zinc soluble. The zinc may then be isolated by means of hydrogen sulfide as recommended by Hibbard.

Theoretical considerations of the mechanism of combination between 8-quinolinol and the ions of heavy metals led Rây and Bose (7, 8) to experiment with other related compounds for use as analytical reagents. Among these was quinaldic acid. These authors obtained excellent results when this compound was used as a precipitant for the gravimetric de-

termination of zinc. Later, they adapted the use of quinaldic acid to a micromethod (5, 6).

The findings of Rây and Bose suggested that it might be possible to prepare a colored derivative of quinaldic acid which not only would precipitate zinc quantitatively but could also be used for a colorimetric determination. Colored derivatives are obtained from many organic compounds upon the introduction of one or more nitro groups into the molecule. This was found to be true of quinaldic acid. The method of Besthorn and Ibele (2) for the preparation of 5-nitroquinaldic acid was employed, and two isomeric compounds were produced, a considerable quantity of 8-nitroquinaldic acid being formed. Only the 5-nitro acid was found to precipitate zinc in weakly acid solutions. This acid possesses a pale yellow color of insufficient intensity for colorimetric measurement. When it is treated with stannous chloride, however, a water-soluble reduction product is formed which has a deep orange color well suited for colorimetric comparisons. The following procedure was devised for the determination of quantities of zinc ranging from 0.05 to 1.00 mg.

### Reagents and Apparatus

The method of Besthorn and Ibele (2) was employed for the preparation of 5-nitroquinaldic acid from quinaldic acid obtained from the Eastman Kodak Company. The compound thus prepared crystallized from water, and after being dried at 105° C. it retained two molecules of water of crystallization. The reagent used in this procedure consisted of 0.75 gram of this compound dissolved in 100 ml. of warm 95 per cent ethyl alcohol. One milliliter of the solution was equivalent to approximately 1 mg. of zinc.

Ammonium hydroxide, approximately 3 *N*, was prepared by diluting 1 part of concentrated ammonium hydroxide (sp. gr. 0.90) with 4 parts of distilled water.

Acetic acid, 50 per cent, was prepared by diluting glacial acetic acid with an equal volume of distilled water.

Stannous chloride solution consisted of 12.5 grams of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in 100 ml. of hydrochloric acid (sp. gr. 1.21) and diluted to 500 ml. The solution was preserved by the addition of a little metallic tin.

Methyl red indicator solution was made by dissolving 0.1 gram of methyl red in 100 ml. of 95 per cent ethyl alcohol.

The colorimeter used was like that devised by Yoe and Crumppler (11), but contained a photoelectric cell circuit of greater sensitivity as suggested by Wood (10).



TABLE I. INFLUENCE OF TIME OF DIGESTION UPON COMPLETENESS OF PRECIPITATION OF ZINC

Digestion Period Min.	Zinc Added Mg.	Zinc Recovered Mg.
10	0.10	0.090
10	0.10	0.080
15	0.10	0.10
15	0.10	0.095
30	0.10	0.10
30	0.10	0.11
24 hours	0.10	0.10
24 hours	0.10	0.095
10	0.50	0.494
10	0.50	0.494
15	0.50	0.499
15	0.50	0.500
30	0.50	0.500
30	0.50	0.501
24 hours	0.50	0.498
24 hours	0.50	0.499

TABLE II. EFFECT OF EXCESS REAGENT ON PRECIPITATION OF ZINC BY 5-NITROQUINALDIC ACID

Excess of Reagent %	Zinc Present Mg.	Zinc Recovered Mg.
25	0.20	0.200
25	0.20	0.198
144	0.20	0.200
144	0.20	0.197
213	0.20	0.200
213	0.20	0.199
340	0.20	0.200
340	0.20	0.202
25	0.50	0.501
25	0.50	0.502
144	0.50	0.502
144	0.50	0.499
213	0.50	0.500
213	0.50	0.500
340	0.50	0.500
340	0.50	0.498

Analytical Procedure

The quantity of zinc to be taken for a determination will vary with the type of colorimeter to be employed. Quantities ranging from 0.05 to 1.00 mg. were easily within the range of the colorimeter described above. The zinc, having been previously separated from interfering substances by a method such as the one suggested by Boggs and Alben (3), was brought into solution by means of hydrochloric acid, and was then determined by the following procedure:

An aliquot containing 0.05 to 1.00 mg. of zinc is pipetted into a 30-ml. beaker. The volume is brought to 5 to 10 ml. by evaporating or diluting as necessary. A drop of methyl red indicator is added and the solution made just alkaline with 3 *N* ammonium hydroxide. Acetic acid is added until the solution is distinctly acid (1 to 2 drops). The solution is heated to near boiling and 5-nitroquinaldic acid solution is added in slight excess of that necessary to bring about complete precipitation. The beaker and contents are allowed to stand on the hot plate for 30 minutes without boiling. The precipitate is filtered off by means of an asbestos filter stick, and the beaker and filter are washed five times with boiling water from a wash bottle. The precipitate is dissolved in 5 ml. of hot stannous chloride solution, and heated to boiling. Any asbestos that may be present is filtered off and the solution is cooled to room temperature, and compared in the colorimeter with standards prepared by the same procedure from solutions containing known quantities of zinc. The standard and unknown must be at the same temperature at the time of reading.

When a photoelectric colorimeter is used for the determination, it is convenient to make use of a graph prepared from readings made on standard solutions. The colorimeter readings in microamperes are plotted as ordinates, and the quantities of zinc employed as abscissas. A curve is thus obtained which may be used for reading off the quantity of zinc corresponding to any reading of the colorimeter. This expedient eliminates the necessity for preparing standards every time that determinations are to be made.

The precision which may be obtained by this method in the measurement of the zinc in standard solutions is illustrated by the close agreement between values in Table II.

Conditions Influencing Precipitation

ACIDITY. The zinc salt of 5-nitroquinaldic acid dissolves readily in solutions of the more highly ionized acids, but remains insoluble in solutions having pH values in the range 2.5 to 8.0.

In order to determine the range of hydrogen-ion concentration within which precipitation might be complete, a series of experiments was carried out with 0.5-mg. portions of zinc in the form of the chloride. A standard solution was prepared by dissolving 1 gram of c. p. metallic zinc in hydrochloric acid and diluting to 1000 ml. One hundred milliliters of this solution were diluted to 1000 ml. and several 5-ml. portions were pipetted into 30-ml. beakers. Various acidities were obtained by adding different quantities of hydrochloric acid, acetic acid, and ammonium hydroxide to different beakers, using methyl orange, methyl red,

and phenolphthalein indicators to cover a wide range of pH values. The zinc was then precipitated and determined by the above procedure. The filtrates from which the precipitates were separated were immediately cooled and their pH values determined employing a glass electrode (Beckman pH meter).

The results obtained are shown graphically in Figure 1. The precipitation of zinc is found to be complete within the range of pH 2.5 to 8.0. The use of acetic acid and methyl red indicator as recommended in the procedure gives acidities lying well within these limits.

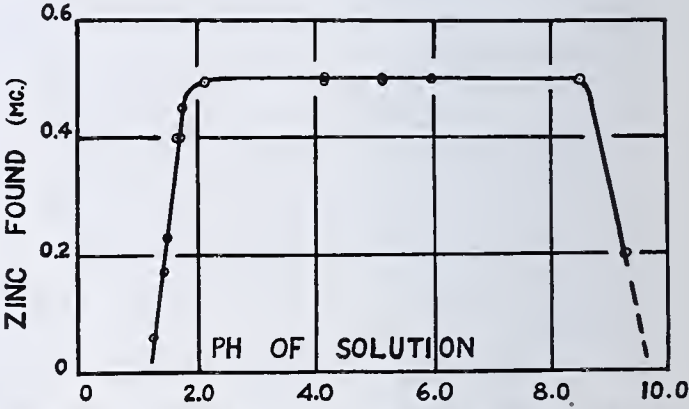


FIGURE 1. INFLUENCE OF HYDROGEN-ION CONCENTRATION ON PRECIPITATION OF ZINC

TIME OF DIGESTION. The time of digestion necessary for complete precipitation was determined as follows:

Two series of solutions of zinc chloride containing 0.5 and 0.1 mg. of zinc, respectively, were treated with an excess of 5-nitroquinaldic acid after adjustment of acidity, and were digested on the steam bath for periods ranging from 10 minutes to 24 hours. The precipitates were then filtered off, and their zinc contents determined as previously described.

The figures in Table I indicate that precipitation had reached a maximum value after digesting for 15 minutes. In most instances the supernatant solutions were still turbid at the end of this time, and digestion for 30 minutes resulted in clear solutions. It might be deemed best, therefore, to digest for 30 minutes to reduce the possibility of fine particles passing through the filter.

ADSORPTION OF EXCESS REAGENT. Two series of precipitations were carried out with 0.5- and 0.2-mg. portions of zinc, with acidities and digestion periods as given in the procedure. 5-Nitroquinaldic acid was added in excesses amounting to 25, 144, 213, and 340 per cent greater than the theoretical amounts needed for complete precipitation. The precipitates were filtered off and determinations made by the procedure given. The results (Table II) show that the precipitates did not adsorb appreciable quantities of the excess



TABLE III. EFFECT OF AMMONIUM CHLORIDE ON PRECIPITATION OF ZINC

NH <sub>4</sub> Cl Concentration <i>N</i>	Zinc Present <i>Mg.</i>	Zinc Recovered <i>Mg.</i>
0.0	0.20	0.195
0.0	0.20	0.200
0.15	0.20	0.200
0.15	0.20	0.200
0.70	0.20	0.200
0.70	0.20	0.198
1.0	0.20	0.193
1.0	0.20	0.190
0.0	0.50	0.500
0.0	0.50	0.497
0.15	0.50	0.500
0.15	0.50	0.500
0.70	0.50	0.503
0.70	0.50	0.495
1.0	0.50	0.475
1.0	0.50	0.480

TABLE IV. EFFECT OF CONCENTRATION OF ACID ON DEPTH OF COLOR

Acid Concentration <i>N</i>	Colorimeter Reading <sup>a</sup> <i>Microamperes</i>	Zinc Equivalence <i>Mg.</i>
0.24	82.1	0.20
0.48	82.0	0.20
0.60	81.8	0.21
0.72	82.0	0.20
0.84	82.1	0.20
1.08	83.0	0.17
1.20	85.5	0.15
1.40	89.5	0.10
0.24	63.8	0.50
0.48	63.6	0.50
0.60	64.0	0.50
0.72	63.8	0.50
0.84	63.6	0.51
1.08	65.2	0.47
1.20	67.0	0.42
1.40	69.2	0.39

<sup>a</sup> Represents per cent of light transmitted by colored solution.

reagent, regardless of the quantity of precipitant used. Evidently the excess of 5-nitroquinaldic acid is readily removed by the hot wash water. The close agreement between these values also indicates the degree of precision obtained with this reagent.

**INTERFERING SUBSTANCES.** Interfering substances are liable to be of frequent occurrence since many metals are precipitated under the conditions of this method. Tests showed that 5-nitroquinaldic acid forms insoluble precipitates with silver, lead, mercury, copper, iron, manganese, cobalt, and nickel in weakly acid solutions. With respect to its nonspecificity as an analytical reagent, 5-nitroquinaldic acid is similar to 8-quinolinol (1).

It is necessary to separate zinc from any or all the metals listed above before an accurate determination can be made by this method. This is best accomplished by means of hydrogen sulfide as already mentioned. The zinc sulfide so obtained is brought into solution by means of hydrochloric acid. It was found that ammonium chloride formed by neutralizing acid in such solutions with ammonium hydroxide may inhibit complete precipitation of the zinc within the digestion period of 30 minutes. Results given in Table III show the concentrations of ammonium chloride that may be tolerated. Complete recovery of zinc may be accomplished in the presence of ammonium chloride in concentrations as high as 0.7 *N* but not from solutions of higher concentration. Before making determinations by this procedure it is best, therefore, to avoid the use of large quantities of acid in dissolving the precipitates of zinc sulfide. Similar concentrations of sodium chloride also inhibit complete precipitation, so that sodium hydroxide offers no advantage over ammonium hydroxide for the neutralization of the acid.

**Conditions Influencing Color Intensity**

High concentrations of acid were found to decrease the depth of color, as shown by Table IV. Portions of 5-nitroquinaldic acid solution equivalent to 0.5 and 0.2 mg. of zinc, respectively, were pipetted to beakers, and the alcohol was evaporated by warming gently. Concentrated hydrochloric acid was added in increments to different beakers, and the solutions were treated with equal quantities of a hot solution of stannous chloride. The resulting solutions were nearly colorless at higher acid concentrations but were distinctly colored at the lower concentrations. Most of the solutions, however, developed full color intensity upon being diluted to volume in the tube of the colorimeter. The results show that the intensity of color was not appreciably influenced by differences in concentration of acid within the range 0.24 *N* to 0.84 *N*. The quantity of hydrochloric acid found adequate for dissolving and reducing the precipitates obtained in this

method gives a normality of 0.24 upon dilution for the colorimeter. Hence, the acidity is sufficiently low for accuracy.

Variation in temperature of the solutions at the time of reading was found to have considerable influence on the depth of color. At high temperatures the solutions are more intensely colored than at room temperature, and considerable error may occur in determinations if readings are made with standard and unknown at different temperatures.

The intensity of color of the solutions of reduced 5-nitroquinaldic acid was found to be independent of the concentrations of stannous chloride over the range 0.075 to 0.40 per cent SnCl<sub>2</sub>·2H<sub>2</sub>O.

The color of the solutions is stable. The solutions tested were found to give the same readings after standing for 24 hours as they gave immediately after reduction.

**Spectral Absorption of the Colored Solutions**

Spectrophotometric measurements made on solutions of 5-nitroquinaldic acid reduced by stannous chloride showed that such solutions absorb light in the visible portion of the spectrum between 4000 and 6000 Å., and transmit almost completely the higher wave lengths. The violet, blue, and lower half of the green bands are absorbed by concentrated solutions, while the upper half of the green band and the yellow and red bands are transmitted. It is apparent, therefore, that filters which transmit the violet, blue, or the lower half of the green bands of the spectrum may be used in colorimeters with this reagent.

**Discussion**

The range of quantities of zinc conveniently determinable by the technic described in the analytical procedure was found to be 0.05 to 1.0 mg. Quantities as large as 2 mg. have been determined by the same procedure. It was necessary, however, to dilute the colored solutions to concentrations suitable for the photoelectric colorimeter. When such dilutions were carried out, an extra 5-ml. portion of stannous chloride solution was added, so that sufficient acid was present to prevent hydrolysis of the stannous chloride. Omission of this precaution sometimes resulted in turbid solutions. The range of quantities of zinc determinable by this method is, therefore, limited to 0.05 to 2.0 mg. Extension of the range to larger or smaller quantities would require further modifications of technic.

5-Nitroquinaldic acid is expensive to prepare by present methods. Quinaldic acid was selling for \$3.60 per 10 grams at the time it was purchased for this work. Since the yield on nitration is less than 50 per cent of the theoretical, the reagent seems rather costly for use other than for microdeter-



minations, although it should serve admirably for gravimetric macrodeterminations. The cost of reagent for a single microdetermination is estimated to be about 2.5 cents, which is not prohibitive.

### Summary

A procedure which has been successfully used for the colorimetric microdetermination of the zinc content of agronomic materials is described. The method is applicable for the determination of quantities of zinc ranging from 0.05 to 1.0 mg.

After a preliminary separation of the zinc from interfering elements, 5-nitroquinaldic acid is used as a precipitating agent. The precipitate is filtered from the excess reagent, and converted into an orange-colored, water-soluble compound by reduction with stannous chloride. The intensity of color is measured by means of a photoelectric colorimeter.

Precipitation of zinc by 5-nitroquinaldic acid is complete within a range of pH 2.5 to pH 8.0 after digestion for 30 minutes. Ammonium chloride and sodium chloride in concentrations greater than 0.7 *N* inhibit the complete precipitation of the zinc.

The intensity of color of the reduction product of 5-nitroquinaldic acid is independent of the acid concentration at acidities lower than 0.8 *N* and of the concentration of stan-

nous chloride. The intensity of color increases appreciably with rise in temperature of the solutions, making it necessary to carry out all readings at the same temperature.

### Acknowledgment

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## A Copper Tube Preheater

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MANY references occur in the literature to the construction and use of preheaters or "catalyzer tubes" for burning oxidizable impurities present in air and commercial oxygen gas. The following is a description of a preheater for

use in microanalyses of carbon and hydrogen. In addition to being very efficient, it has the advantages of simplicity, extreme ruggedness, and low cost of construction.

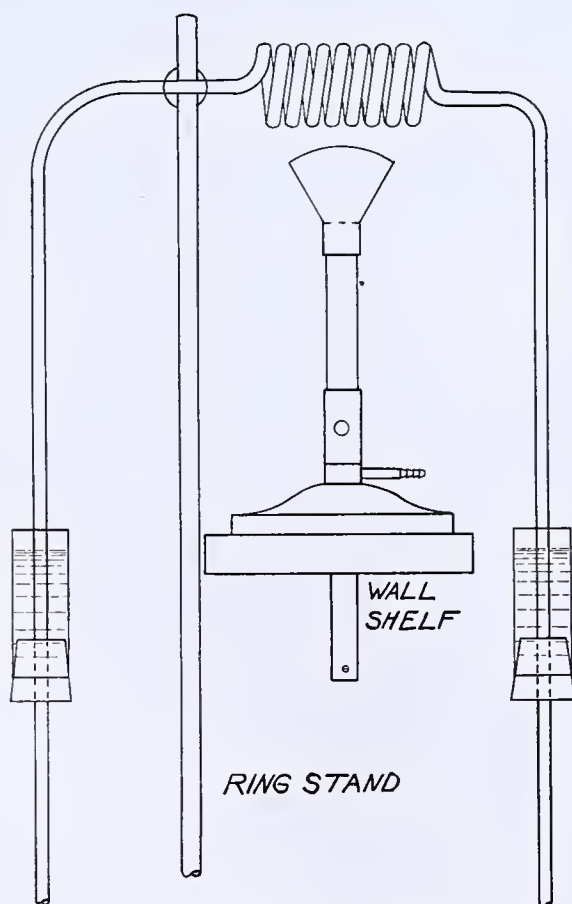
The preheater is made from a 1-meter length of commercial copper tubing approximately 5 mm. in outside diameter with walls 1 mm. thick. Because it has been found convenient to stand the preheater on the shelf at the back of the desk, this length is greater than may otherwise be needed. At a distance of 30 cm. from the inlet end (see figure), the tubing is wound several times around a pipe of small diameter (1 cm.), forming a compact coil. The coil is clamped in a horizontal position at burner height. At either end of the coil, the tubing is bent downward at right angles and slightly towards the front of the desk in order to clear the shelf. The inlet and exit ends are attached with rubber connections to the pressure regulator and purifying line, respectively. To prevent the rubber connections from being overheated, the two ends are surrounded by water jackets. These consist of 6-cm. lengths of 20-mm. glass tubing fitted at their lower ends over rubber stoppers of proper size. The jackets are conveniently filled with water from a wash bottle, once a week being sufficiently often even when the apparatus is in constant use.

The coil is heated with a Pittsburgh burner and wing top. When first prepared, after flushing out with grease solvents, the copper tube is heated to redness over its entire length with a stream of oxygen passing through. On further heating the coil becomes filled with copper oxide scale, thus providing efficient contact with the entering gas.

Two such preheaters have been in daily use in this laboratory for over 6 months without developing leaks through corrosion at the heating surface.

In order to test the efficiency of this type of preheater, a number of blanks were run using compressed air directly from the laboratory line. Although this air was saturated with colloidal oil and other organic impurities, negligible blanks were obtained. This is probably the most rigorous test possible of the efficiency of the preheater in converting the organic vapors into absorbable products.

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# The Cathode Ray-Tube Polarograph

## Theory of Method

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THE polarograph as developed by Heyrovský and his co-workers is an instrument well known to electrochemists and analysts. The theory and applications have been summarized in several monographs (1, 2). The recording of current-potential curves of a dropping mercury electrode may be accomplished in a number of ways. Heyrovský gives adequate reasons for preferring the photographic method, such

as performance of the record, etc. It would seem natural to utilize the cathode ray oscillograph for this purpose, but in practice a number of difficulties arise. Oscillograph practice requires rapid recurrence of the phenomenon if a persistent stationary image is desired. It is true that transient images can be photographed, but this procedure would nullify the advantage of a continuous picture of what is going on. If we attempt to sweep through the range of potentials very rapidly in order to produce a persistent stationary pattern, the question arises whether the electrode equilibria can keep pace with the rapidly changing potentials.

The authors have found a solution to this problem and the instrument based on this method yields values identical with those based upon the conventional Heyrovský method.

### Theory

Let curve *OAHBC* of Figure 1 represent an idealized Heyrovský polarogram for a certain ion. The potential, *V*, corresponding to point *H*, is the *Halbwellenpotential* and represents a characteristic identifying value, for the given ion. Now imagine a small sinusoidal alternating potential of peak value,  $\Delta V$ , applied to series with the main potential, *V*. The current, *I*, will now vary about the mean value, *H*, to produce a wave, *S*, of the same wave form and frequency, but with an amplitude which depends upon the steepness of curve *AHB*. If the main direct current potential, *V*, is now shifted the sine wave, *S*, will become distorted at its upper or lower portion because of intersection with the nonlinear portions of the curve at *B* or *A*. If this curve, *S*, is continuously viewed on an oscillograph screen it will be almost perfectly sinusoidal and undistorted when and only when *V* has

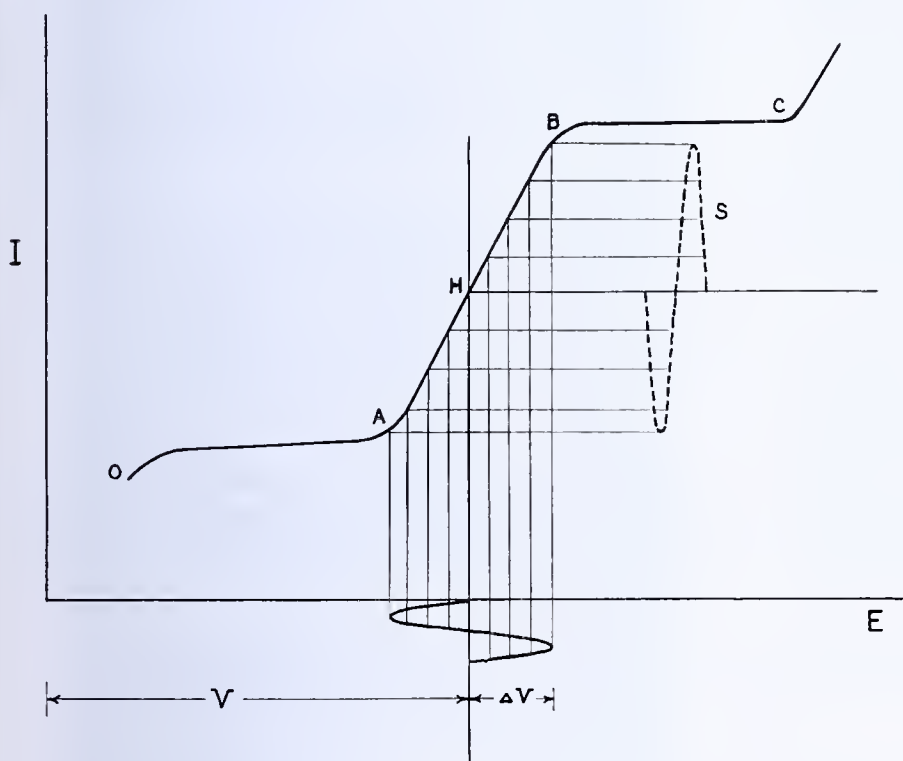


FIGURE 1

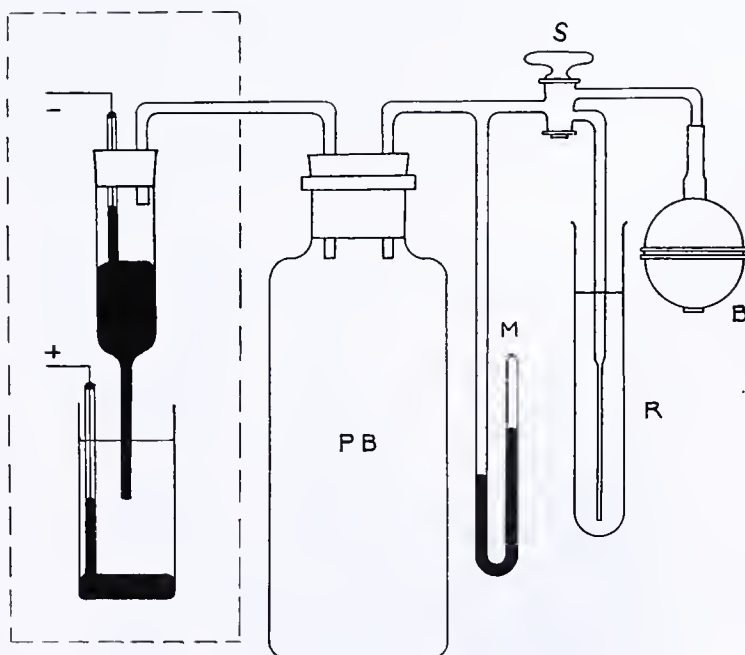
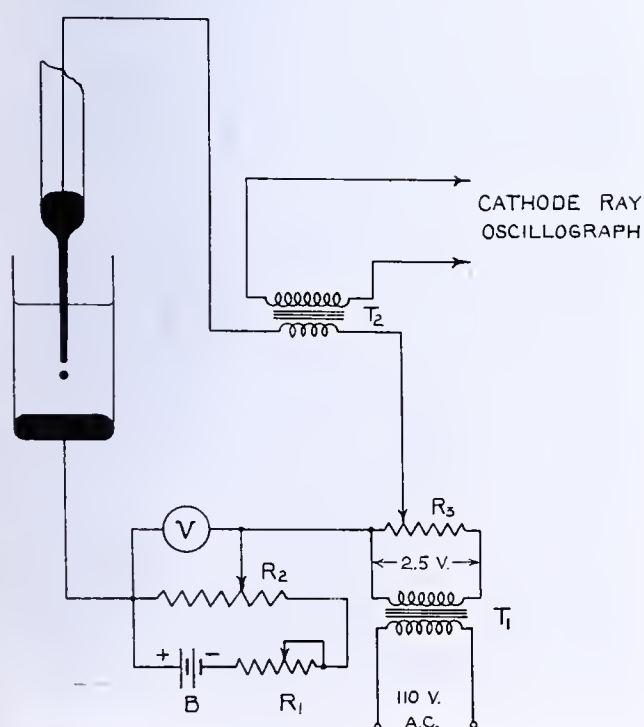


FIGURE 2. CIRCUIT (LEFT) AND DIAGRAM OF APPARATUS (RIGHT)



a value corresponding to the mid-point of the current-potential curve (at  $H$ ). Conversely, the appearance of such undistorted waves, as  $V$  is varied from zero to the maximum value of deposition potentials, will serve to detect and identify the characteristic potentials.

### The Instrument

The circuit is shown in Figure 2, left. Battery  $B$  supplies the potentials through regulating resistor  $R_1$  and voltage divider  $R_2$ . The voltmeter,  $V$ , indicates the applied potential. The small alternating potential in series with the direct current potential is supplied by step-down transformer  $T_1$  and voltage divider  $R_3$ . The lead to the dropping mercury cathode passes through the high-gain, low primary-impedance transformer,  $T_2$ . The secondary of this transformer is connected to the vertical deflector plates of the cathode ray oscillograph. If the oscillograph is not provided with a built-in amplifier or one of sufficient gain (3000 to 5000  $\times$ ) it must be preceded by a voltage amplifier stage. The horizontal deflector plates are driven by the usual sweep circuit and in most cases means are provided for locking in the sweep with the phenomenon under investigation (synchronizing control).

The authors have eliminated the customary leveling bulb for supplying mercury to the dropping electrode in the interest of compactness and convenience of manipulation and to facilitate careful electrical shielding of the electrode assembly.

Figure 2, right, shows a simple arrangement of pressure bottle  $PB$ , rubber bulb  $B$ , and two-way stopcock  $S$  with a micro bubble regulator,  $R$ . Manometer  $M$  gives a rough indication of the driving air pressure. Actually, the rate of dropping of mercury is the best criterion of satisfactory operation, and this is quickly adjusted by means of the stopcock by-pass. Since very little mercury is used, the air reservoir requires very infrequent attention.

Figure 3 shows a photograph of the instrument. The oscillograph is on the right. The main case on the left contains the circuit and controls. The voltmeter indicates the critical direct current potentials. The left-hand dial controls the voltage divider,  $R_2$ . The right-hand dial,  $R_3$ , governs the magnitude of the alternating current potential. Toggle switches are provided for the battery and alternating current supply. The small copper case mounted on the right side of the instrument contains the electrode assembly and can be tightly closed by means of a copper door. The electrode connections pass directly through the wall through insulated connectors ("banana plug" type). The case is grounded during operation. Connection to the oscillograph is made through shielded cable. Reasonably careful shielding and the absence of loose, rambling wires are essential for satisfactory operation.

### Operation

A typical polarogram as obtained by this instrument is shown in Figure 4. In this case the solution contained a small amount of cadmium ion (5 mg.), 0.002  $M$ . At an applied potential of 0.63 volt the oscillograph pattern is as shown in  $a$ . Potentials slightly less than this value yield the distorted curve,  $b$ , whereas at slightly higher potentials another distorted curve,  $c$ , results. This behavior is explained in the

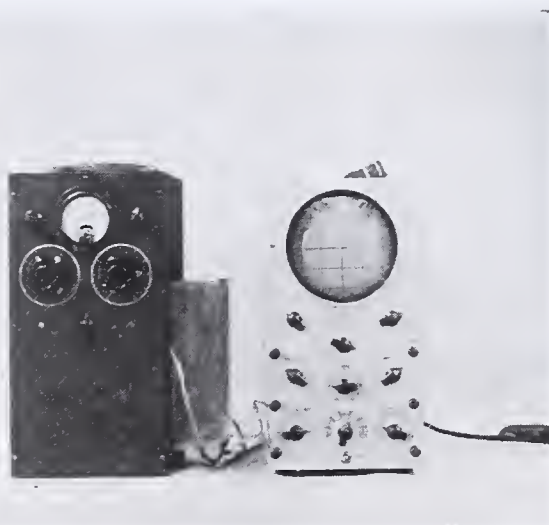


FIGURE 3

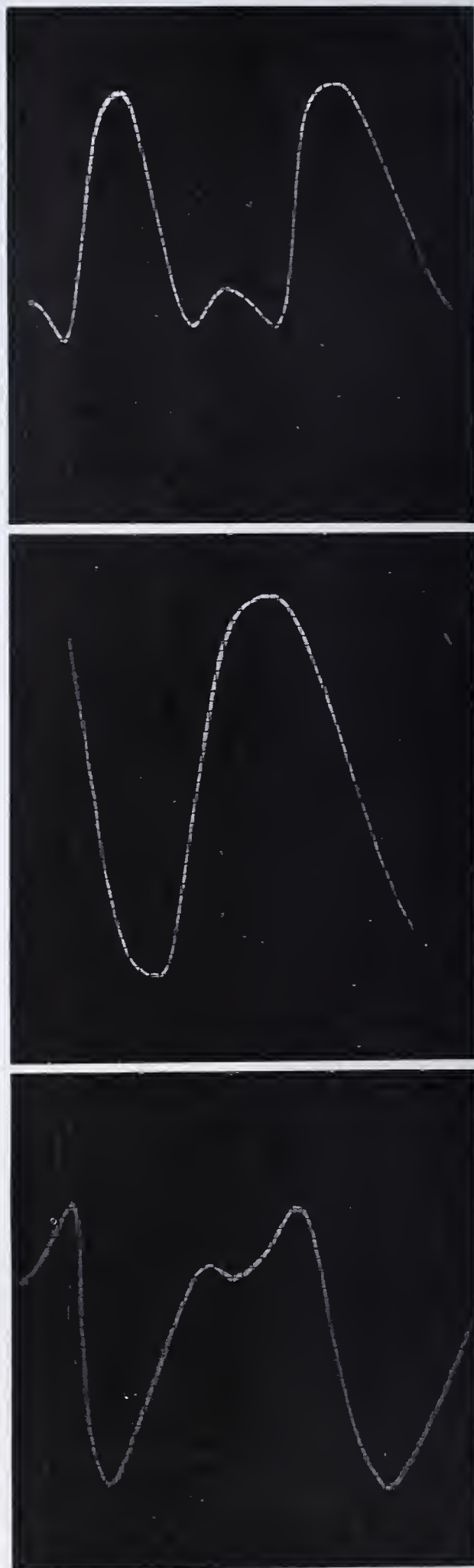


FIGURE 4. TYPICAL POLAROGRAM



discussion of Figure 1. On a complete analysis the operator merely increases the potential,  $V$ , manually from zero to the maximum and notes the potentials at which symmetrical waves appear. The process can be repeated as often as desired. For feeble curves (traces of ion) the gain control may be stepped up in order to miss none. Under these circumstances the maxima due to large amounts of other ions will produce high deflections, beyond the edge of the screen, but the instrument is not damaged as a delicate galvanometer would be.

The entire pattern disappears when a mercury droplet falls from the capillary. A new curve appears almost immediately, and the momentary interruption is not disturbing, inasmuch as the general technic requires fairly slow dropping rates.

The observed potentials are very reproducible and vary by only a few millivolts—0.627 to 0.629 in the above case. Furthermore they are identical with the values obtained in the conventional way—with a voltage divider and galvanometer.

In all cases in which the new instrument was compared with the "manual" method it was absolutely necessary to correct the observed potentials for the anode potential as measured against the solution with a calomel electrode in the conventional way. Authorities (1, 2) agree that this is necessary to obtain the standard value for each ion as recorded in the literature. Thus for zinc ion (0.001  $M$ ) the authors observed a value of  $-1.110$  volts, and the anode potential correction was  $0.041$  volt yielding  $-1.069$  volts for the *Halbwellenpotential*. The accepted value is  $-1.06$  volts.

### Discussion

So far no mention has been made of the quantitative aspects of the instrument. Reference to Figure 1 will show that the final deflection of the cathode ray beam at the *Halbwellenpotential* depends upon the gain of the amplifier, the value of

$V$ , and the height of the "Heyrovský curve" for the particular ion under observation. The gain of the amplifier may be held constant and  $\Delta V$  adjusted to some predetermined value. Investigations are in progress for the determination of suitable values of the voltage under various conditions of operation, so that quantitative estimation may be accomplished with the instrument.

The complete instrument, including the oscillograph but not labor, costs \$150.

### Summary

Current voltage curves taken with an oscillograph using a small series alternating current potential yield patterns which are interpretable on the basis of the conventional Heyrovský method.

The polarograms are viewed continuously and require no photographing or recording.

The actual identification is in terms of the same potentials used by the classical methods.

The introduction of the small alternating current component does not give rise to any complications; the observed values are the same as those obtained with direct current.

The analysis can be repeated indefinitely and the results are continuously visible to the operator.

Sensitivity control is not hampered by possible damage to the recording instrument.

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## Electrolytic Silver Wool in the Filling of Microcombustion Tubes

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IN PREPARING the universal combustion tube filling of Pregl for use in carbon and hydrogen analysis, it is generally recommended (2, 3) that loosely wound silver wire rolls or wads be used. There are obvious mechanical difficulties in this procedure in preparing a closely packed and uniformly distributed filling, and in addition the wire does not offer the maximum surface per unit weight. Recently Elek (1) has advocated the use of rolls of silver gauze because of their greater surface.

It has been found in this laboratory that a "silver wool" produced by electrolysis of metallic silver has several advantages over silver wire. Finely divided silver wool may readily be prepared electrolytically according to well-known methods for purifying silver. A description of a simple electrolytic cell is given by Richards (4). By varying the current through the cell, the crystal size of the deposit can be controlled. In this way crystals have been obtained having a diameter of  $0.005$  to  $0.05$  mm. and length of  $3$  to  $8$  mm. When removed from the electrolytic cell, the crystals are in the form of closely interwoven clusters, and are conveniently handled with pincers in filling the combustion tube. The interwoven clusters facilitate the uniform packing of the tube. Satisfactory

results are obtained without the preliminary ignitions in hydrogen and oxygen, thus saving time.

In general 2 to 3 grams of the crystals are sufficient where 4 to 5 grams of wire (2) are needed. Such crystals present a much greater surface than silver wire of the same dimensions, owing to many imperfections visible under the microscope. Because of the greater surface, the silver wool often outlives the rest of the tube filling.

Thus the qualities attributed to electrolytic silver wool are such as to warrant its preparation and use in microchemical laboratories in preference to the wire form.

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RECEIVED February 14, 1938.



# Mechanism of Absorption of Oxides of Nitrogen by Lead Peroxide in Microcombustions

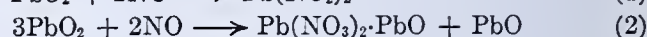
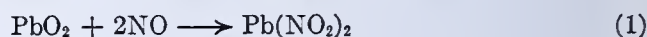
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IN CONNECTION with the direct gasometric microdetermination of oxygen in nitrogen-containing organic compounds, developed in this laboratory (14), it was necessary to make a study of the reaction which occurs when oxides of nitrogen, formed during the combustion of such substances, are absorbed by the lead peroxide present in the combustion tube. It is the purpose of this paper to describe the quantitative study made of the reaction of nitric oxide and also nitrogen peroxide with lead peroxide.

There is very little information in the literature regarding the specific oxides of nitrogen which are formed during the combustion of nitrogen-containing compounds. Some investigators (2, 4, 5, 11, 12, 16) believe nitrogen peroxide is the ultimate oxide formed, whereas others (15, 17) favor nitric oxide and still others (21) believe that nitrous oxide is also likely to be present. Many other investigators make no attempt to distinguish between these oxides, and in discussing their reactions merely refer collectively to oxides of nitrogen.

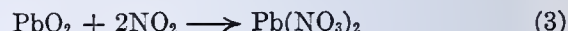
The literature is likewise not specific as to the mechanism of the reaction between the various oxides of nitrogen and lead peroxide. Dennstedt and Hassler (5) claim that nitric oxide can pass over lead peroxide without being absorbed, whereas Auden and Fowler (1) state that a basic lead nitrate is formed, the reaction starting at a temperature as low as 15° C., and attaining a maximum above 130° C., with only traces of nitrite being formed. Sabatier and Senderens (23) demonstrated that nitric oxide on reaction with metallic peroxides formed nitrogen peroxide, the metallic peroxide being reduced.

In aqueous suspension and in the absence of air they claimed that nitric oxide and lead peroxide first formed lead nitrite, which was later converted to a basic nitrite. Moser, however (19), illustrates the reaction between nitric oxide and lead peroxide with the following equations:



Müller and Barck (20) state that nitric oxide is completely absorbed by lead peroxide at room temperature, forming lead nitrite, as in Equation 1, and that at temperatures above 200° C. oxygen begins to be liberated from the lead peroxide. Lindner (17) found that at 180° C. 0.465 gram of lead peroxide absorbed nitric oxide at first rapidly and then more slowly, and after 6 days had taken up 32 cc. According to Equation 1 the lead peroxide should have absorbed 87 cc., and, according to Equation 2, 29 cc.

Kopfer (16), Dennstedt and Hassler (4), Friedrich (11), and Hermann (12) believe that nitrogen peroxide reacts with lead peroxide, forming lead nitrate according to the following equation:



The work to be described was undertaken because the literature failed to yield specific information, required in connection with the investigation previously mentioned, regarding these questions.

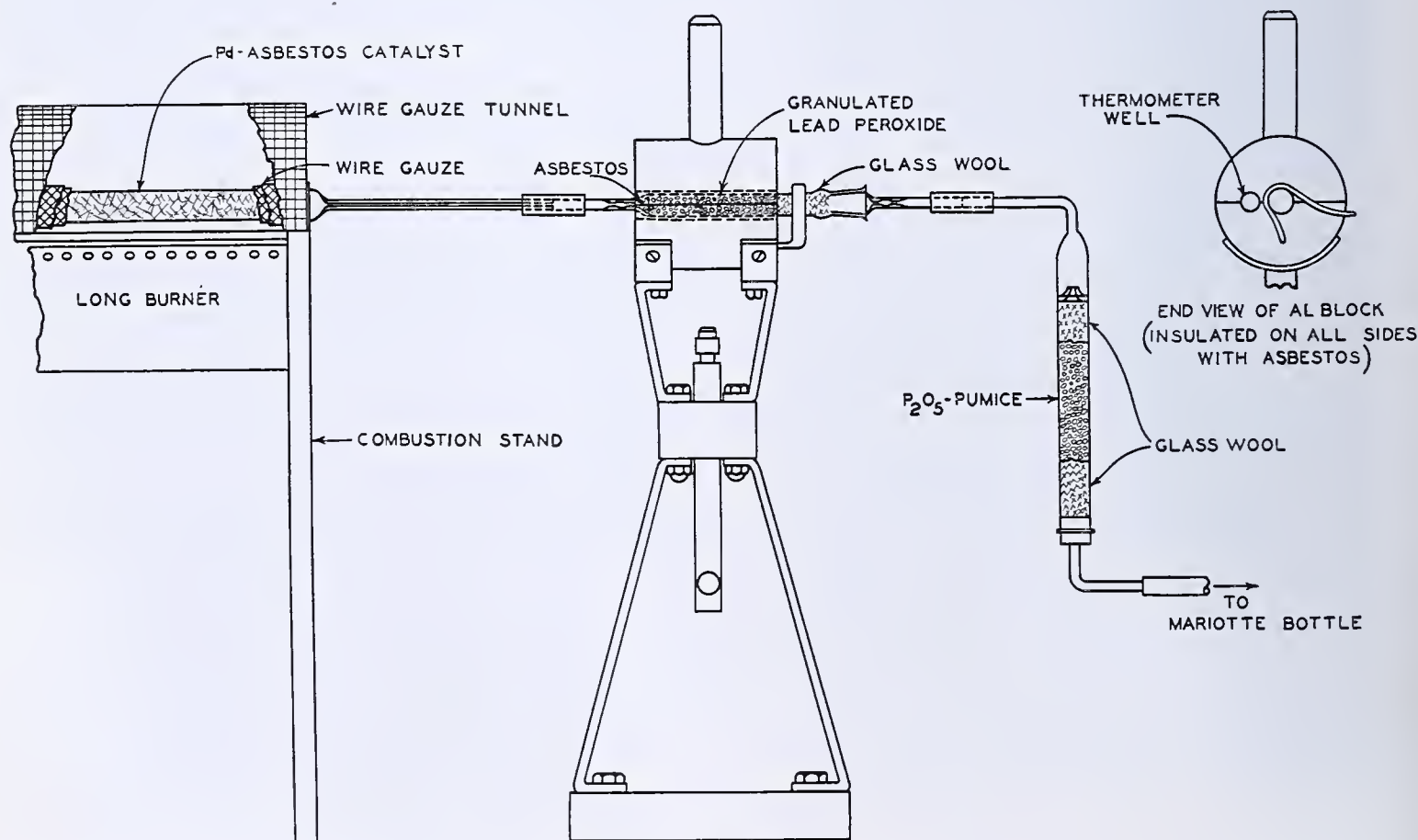


FIGURE 1. THE COMBUSTION TRAIN



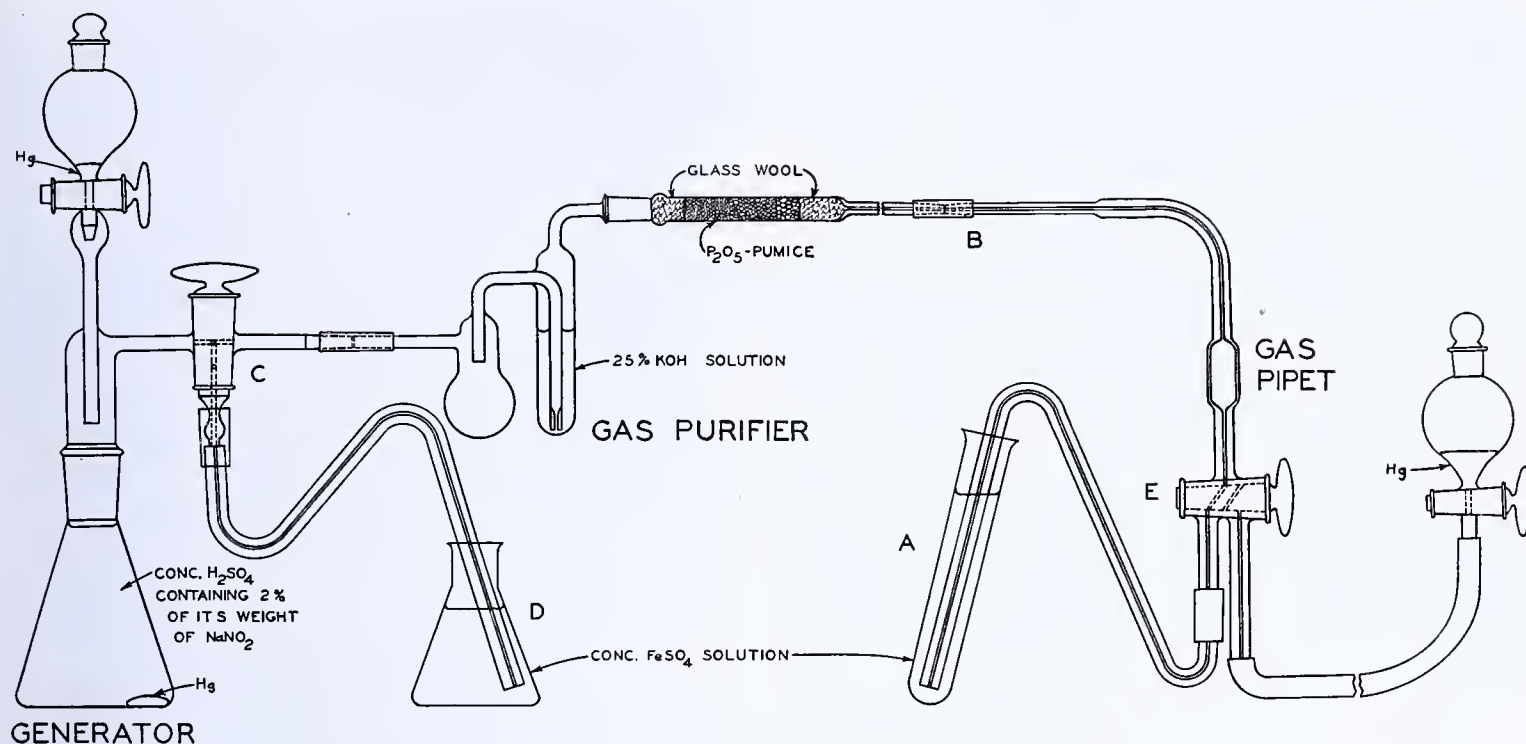


FIGURE 2. APPARATUS FOR PREPARATION OF NITRIC OXIDE

The combustion train (Figure 1) was identical to that devised by Pregl for the carbon and hydrogen microdetermination, except that the side-arm combustion tube had an 8-cm. 0.1-mm. capillary sealed to the exit end. The purpose of this capillary was to transfer the effluent gases, as rapidly as possible, to the weighed micro absorption tube containing purified lead peroxide which was kept at a temperature of about 185° C. by means of an aluminum block heated by a microburner. The gas flow was maintained at 3.0 to 3.5 cc. per minute by means of the pressure regulator and Mariotte bottle.

In the experiments using nitrogen for sweeping, the pressure regulator and bubble counter were filled with the sodium  $\beta$ -anthraquinone sulfonate-sodium hydrosulfite mixture recommended by Fieser (10) for removing oxygen. In filling the gasometer with nitrogen (water pumped), the gas was taken from a high-pressure cylinder and passed through a Milligan gas-washing bottle containing the oxygen absorbent. When oxygen was used for sweeping, the pressure regulator was filled with dilute potassium hydroxide and the bubble counter with 40 per cent potassium hydroxide. From the bubble counter the gases traversed a small U-tube, containing Ascarite and  $P_2O_5$ -pumice, and then entered the side arm of the combustion tube. The combustion tube contained only a 40 per cent palladium-asbestos catalyst, the same that was used in the previous work on the simultaneous determination of carbon, hydrogen, and oxygen (13). No silver was present in the combustion tube, as statements have appeared in the literature (3, 9), although unconfirmed (4, 7, 12, 20), that silver is capable of reducing oxides of nitrogen to elementary nitrogen.

### Preparation of Nitric Oxide

The nitric oxide was prepared by the method of Emich (6) in the apparatus illustrated in Figure 2. In the first work the air in the apparatus was displaced by generating nitric oxide for some time, the waste gas being absorbed in concentrated ferrous sulfate solution in tube A. In the later work the air in the apparatus was removed by evacuating the entire generator and purifying train with a water pump connected through a large U-tube, containing phosphorus pentoxide, attached at B. Nitric oxide was then generated until it had displaced the vacuum. The apparatus was again evacuated and refilled with nitric oxide before the gas pipet was attached. Then the nitric oxide was passed through the calibrated gas pipet (volume = 2.003 cc.), for some time before taking the experimental sample. The nitric oxide was absolutely colorless.

### Combustion Procedure

Before starting the actual experiments the lead peroxide absorption tube was conditioned by placing it in the heated aluminum block and passing nitrogen (or oxygen) through it for some

time. Then, using technic identical to that of an actual run, but with no nitric oxide added, wiping-weighing experiments were made so as to determine the weight characteristics of the absorption tube. The weight of the absorption tube could be duplicated to within  $\pm 0.003$  mg. in these blank determinations. In these experiments the absorption tube was placed in the heated aluminum block and connected to the combustion train and the gas was allowed to flow through it for 45 minutes after first passing through the heated combustion tube. Then the aluminum block was removed and the absorption tube allowed to cool for 10 minutes, with the gas still passing through it, after which it was disconnected from the combustion train, taken to the balance room, wiped, fitted with tight-fitting pins to hinder diffusion and allowed to stand outside the balance for 10 minutes, then placed in the balance and weighed at the end of an additional 5 minutes.

In an actual experiment the combustion tube was heated and gas passed through it for some time. Then the absorption tube was put into the heated aluminum block and attached to the combustion train, and the procedure described above was followed, so as to get the initial weight of the absorption tube. During this time the nitric oxide generator was made air-free. After being weighed the absorption tube was placed in the heated aluminum block and connected to the combustion train, but the water from the Mariotte bottle was not started until later. The atmospheric pressure and temperature in the immediate vicinity of the gas pipet were read, the stopcock on the latter was closed, and the pipet was rapidly disconnected from the generator and attached to the front end of the combustion tube by means of a rubber stopper. During the experiment the generator was stoppered at B and stopcock C turned so that the nitric oxide, which continued to generate slowly, went to waste and was absorbed in ferrous sulfate solution in flask D.

The siphon tube of the Mariotte bottle was then lowered, so that the flow of gas started and was maintained at the proper rate. Then the leveling bulb was raised to a height of 7 to 8 cm. above the horizontal arm of the pipet and the scratched stopcock, E, was opened cautiously so that the mercury entered the pipet and slowly and regularly displaced the nitric oxide, 10 to 15 minutes usually being required. When the mercury reached the end of the horizontal capillary of the pipet, which extended into the combustion tube, stopcock E was closed. The nitric oxide which had entered was then swept through the combustion tube and into the absorption tube and continued until 45 minutes had elapsed from the time of starting the nitric oxide. At the end of this time the aluminum block was removed and gas passed for an additional 10 minutes, after which the absorption tube was removed, taken to the balance room, wiped, fitted with tight-fitting pins, and weighed after the appropriate interval. A total of 150 to 175 cc. of gas was passed through the absorption tube during the 55-minute interval.



During the period while the absorption tube was standing next to the balance, the gas pipet was transferred from the combustion tube back to the generator, the leveling bulb lowered, stopcock *E* opened, and the mercury displaced by nitric oxide, the mercury level being finally carefully adjusted to the top of stopcock *E*; the latter was then turned so that the nitric oxide continued to pass to waste and was absorbed in ferrous sulfate solution in tube *A*.

After the increase in weight of the absorption tube had been determined it was again placed in the heated aluminum block and connected with the combustion train. The atmospheric pressure and temperature of the pipet were again read, stopcock *E* was closed, the pipet was transferred to the front of the combustion tube, and the entire experiment was repeated. Besides the experiments made with the combustion tube heated, several runs were made with the combustion tube at room temperature.

### Nitric Oxide Swept with Nitrogen

The results of the above experiments are shown in Table I. The most striking fact brought out in the table is the extremely small increases in weight of the absorption tube in the early experiments and also the manner in which these increases practically double in successive experiments made on the same day until a practically constant value of 64 to 65 per cent is reached after Experiment 10.

TABLE I. NITRIC OXIDE-LEAD PEROXIDE REACTION

Expt. No.	Time for addition Min.	Pressure Mm. Hg	Nitric Oxide		Weight added Mg.	Increase, PbO <sub>2</sub> Absorption Tube Mg.	%
			Temp. ° C.	Volume added N. T. P. Cc.			
1	10.5	731.3	25.7	1.762	2.361	0.024	1.02
2	7	732.2	25.0	1.768	2.369	0.048	2.03
3	10	732.5	25.0	1.769	2.370	0.104	4.39
4	7	736.5	23.5	1.787	2.395	0.090	3.76
5	7	736.4	23.8	1.785	2.392	0.183	7.65
6	12	741.0	24.9	1.790	2.399	0.227	9.46
7	18	740.6	25.9	1.783	2.389	0.499	20.89
8	14	740.4	26.3	1.780	2.385	0.709	29.73
9	23	740.2	27.0	1.775	2.379	0.824	34.64
10	14	740.2	28.0	1.769	2.371	1.262	53.23
11	13	739.2	29.4	1.759	2.357	1.561	66.23
12	12	738.0	28.0	1.764	2.364	1.481	62.65
13	22	738.2	28.6	1.761	2.360	1.412	59.83
14	12	738.0	29.5	1.755	2.353	1.515	64.39
15	20	740.5	28.9	1.765	2.365	1.539	65.07
16	10	740.4	30.0	1.758	2.356	1.511	64.13
17	11	739.8	30.9	1.752	2.347	1.490	63.49
Combustion Tube at Room Temperature							
18	10	738.2	26.2	1.775	2.379	1.606	67.51
19	13	738.0	27.7	1.766	2.367	1.503	63.50
20	14	737.6	29.0	1.757	2.355	1.833	77.83

<sup>a</sup> The horizontal spaces separate experiments made on succeeding days.

A possible explanation of this behavior is that at the start of the experiments the hot palladium-asbestos catalyst (maximum temperature about 600° C.) almost completely reduces the nitric oxide to nitrogen, so that very little of it reaches the lead peroxide. As more nitric oxide is passed through the catalyst the latter, owing to oxidation, gradually loses its reductive ability, so that after Experiment 10 the nitric oxide is probably passing through practically unchanged. Calculation shows that in Experiments 1 to 10 sufficient nitric oxide could theoretically have oxidized, to palladous oxide, over 20 per cent of the palladium present which is then no longer effective in reducing nitric oxide. Twenty per cent possibly represents the amount of the total palladium present which is sufficiently exposed to undergo a surface reaction. It is known that palladium undergoes oxidation at temperatures of 600° to 700° C. (18) and that nitric oxide is an oxidizing agent at these temperatures and, when reduced by many metals, is quantitatively converted to nitrogen (8, 22). At the start of the experiments the palladium-asbestos had a gray, metallic appearance and after the experiments were completed it was brown, indicating oxidation. The following experiments support the above explanation:

After Experiment 8, 17.2 mg. (12.8 cc. N. T. P.) of nitric oxide are unaccounted for. If this amount had passed through

the lead peroxide tube it should have reached the water in the Mariotte bottle and then been oxidized to higher oxides of nitrogen by the air present in the top of the bottle. These, in turn, should have been detectable by the sensitive diphenylamine test. However, such a test, made after completion of Experiment 8, was negative.

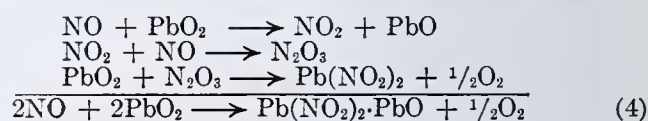
Experiments 18, 19, and 20 were made with the combustion tube at room temperature. The amount of nitric oxide absorbed by the lead peroxide in each of these experiments was essentially the same as when the combustion tube was heated. The variations in the results of the room temperature experiments can probably be ascribed to adsorption of nitric oxide on the oxidized palladium-asbestos.

TABLE II. NITRIC OXIDE-LEAD PEROXIDE REACTION

Expt. No.	Nitric Oxide		Found Theoretical %
	Theoretical Mg.	Found Mg.	
11	1.729	1.561	90.30
12	1.734	1.481	85.42
13	1.731	1.412	81.58
14	1.725	1.515	87.81
15	1.735	1.539	88.72
16	1.728	1.511	87.44
17	1.722	1.490	86.55
Combustion Tube at Room Temperature			
18	1.745	1.606	92.05
19	1.736	1.503	86.60
20	1.727	1.833	106.13

From these results it can be inferred that the catalyst is no longer effective and, whether hot or cold, permits the nitric oxide to pass through it without reaction. It is therefore concluded that when successive experiments yield practically constant increases in weight of the lead peroxide tube, beginning with Experiment 11, the palladium-asbestos catalyst has ceased to react and allows the nitric oxide to enter, unchanged, into the lead peroxide tube.

In searching for an equation to express quantitatively the results of these reactions it was obvious that Equations 1 and 2, given by Moser, are inadequate, since in no case was the increase in weight of the lead peroxide tube equal to the weight of nitric oxide added. The only quantitative data which could be found in the literature for the reaction between nitric oxide and lead peroxide, up to saturation, were those given by Lindner (17), who also pointed out that Moser's equations did not fit his data. Taking Lindner's data and applying them to various equations finally yielded the following:



In this equation a half molecule of oxygen is liberated for each pair of nitric oxide molecules which react with the lead peroxide. Using this equation and calculating the "apparent" amount of nitric oxide which would be absorbed by the 0.465 gram of lead peroxide used by Lindner gives 32.6 cc.; Lindner found that 32 cc. were absorbed.

The above equation includes the mechanism suggested by Sabatier and Senderens and also yields the final product which they claim is formed in aqueous suspension. While Auden and Fowler claim that a basic lead nitrate is formed in this reaction, they give no details of their experimental procedure. Since lead nitrite is said to be extremely unstable, it is possible that during the isolation of their product the basic nitrite was oxidized to basic nitrate. Finally, the formation of a basic nitrite could account for the harmful influence nitric oxide has upon lead peroxide in its effect on the determination of carbon, as pointed out by Lindner.

Using the above equation for the calculation of the results and including only data in which the nitric oxide absorption had become constant, yield the results shown in Table II. The fact that, with the exception of the last experiment, the percentages do not reach 100, may be explained as due to in-



complete absorption of the nitric oxide by the lead peroxide. The incomplete absorption of nitric oxide by lead peroxide, when in contact for relatively short periods, agrees with qualitative statements of previous investigators. The value in excess of 100 per cent, obtained in Experiment 20, is probably due to adsorption effects.

Nitric Oxide Swept with Oxygen

In these experiments the procedure was exactly the same as described above except that oxygen was used for sweeping. When the nitric oxide was added to the combustion tube from the gas pipet brown vapors could be seen at the point where the two gases came into contact. These experiments have much more significance, as regards comparison with conditions which actually exist during a combustion, than those already described, since nitrogen peroxide is a much more likely end product from a properly conducted combustion of a nitrogen-containing compound (14) than is nitric oxide.

Results

The results of the nitrogen peroxide experiments are given in Table III. Before starting this series of experiments the lead peroxide absorption tube was conditioned with oxygen as already described. In contrast to the nitric oxide experiments, the first experiment with nitrogen peroxide yields an increase in weight of the lead peroxide tube which is of the same order of magnitude as the later ones.

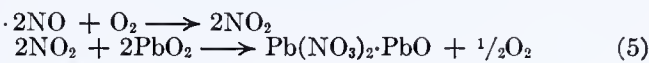
TABLE III. NITROGEN PEROXIDE-LEAD PEROXIDE REACTION

Expt. No.	Nitric Oxide							
	Time for addition	Pressure	Temp.	Volume added	Weight added	NO <sub>2</sub> Weight added	Increase, PbO <sub>2</sub> Absorption Tube	
	Min.	Mm. Hg	° C.	N. T. P. Cc.	Mg.	Mg.	Mg.	%
1	11	744.8	32.1	1.756	2.354	3.609	3.057	84.70
2	14	743.8	33.7	1.745	2.339	3.585	3.026	84.40
3	11	743.6	32.9	1.749	2.344	3.594	3.132	87.15
4	10	742.6	29.8	1.765	2.365	3.626	3.034	83.68
5	15	741.8	30.2	1.760	2.359	3.617	3.024	83.61
6	10	740.8	31.0	1.753	2.350	3.603	3.077	85.41
Combustion Tube at Room Temperature								
7	12	737.8	28.8	1.759	2.357	3.614	2.627	72.69
8	12	737.6	29.3	1.756	2.353	3.607	3.108	86.16
9	10	736.5	30.3	1.747	2.342	3.590	3.262	90.86
Combustion Tube Heated after Absorption Tube Reattached; No NO Added								
10	..	..	..	..	..	..	0.962	..

After obtaining the above data the next step was to find an equation which would fit. Since the increase in weight of the lead peroxide tube never equaled the weight of nitrogen peroxide added, which was recently confirmed by Friedrich (11), it was apparent that the reaction is not as simple as Equation 3 above, given by Dennstedt, would indicate. Kopfer and also Dennstedt state that (neutral) lead nitrate is formed according to Equation 3, but they give no experimental proof of the fact, although Dennstedt claims that the lead nitrate could be extracted from the lead peroxide with a 33 per cent alcohol solution and the weight of the material thus extracted agreed with the increase in weight of the lead peroxide when calculated as lead nitrate. However, he did not prove that the residue left on evaporation of the extract was really lead nitrate. Hermann (12) pointed out the possibility of a reaction between lead peroxide and alcohol during this extraction process.

After the entire series of experiments was completed, the water in the Mariotte bottle was again tested for oxides of nitrogen with diphenylamine-sulfuric acid and only a trace found to be present. However, on dissolving the contents of the P<sub>2</sub>O<sub>5</sub>-pumice protection tube in water, the solution gave a strong test for oxides of nitrogen.

The following equation was found to explain satisfactorily the reaction which occurred between the nitrogen peroxide and the lead peroxide:



According to this equation the net gain in weight of the lead peroxide corresponds to about 85 per cent of the total weight of nitrogen peroxide added. Table IV gives the results of calculations based on the above equation. Since the first experiment made with the combustion tube at room temperature (Experiment 7) yielded a value lower than the rest, it was suspected that nitrogen peroxide or nitrogen tetroxide was adsorbed or absorbed on the catalyst. In order to verify this suspicion the lead peroxide tube, after being weighed at the end of Experiment 9, was again attached to the combustion tube which was then heated and, after it had attained its full temperature, oxygen was passed through as in a normal experiment. The lead peroxide tube gained 0.962 mg., which is somewhat higher than the deficit shown by Experiment 7 but definitely shows that nitrogen peroxide was present in the combustion tube.

TABLE IV. NITROGEN PEROXIDE-LEAD PEROXIDE REACTION

Expt. No.	Nitrogen Peroxide		Found
	Theoretical	Found	
	Mg.	Mg.	Theoretical %
1	2.982	3.057	102.5
2	2.962	3.026	102.2
3	2.969	3.132	105.5
4	2.995	3.034	101.3
5	2.988	3.024	101.2
6	2.976	3.077	103.4
Combustion Tube at Room Temperature			
7	2.986	2.627	87.98
8	2.980	3.108	104.3
9	2.966	3.262	110.0

In order to get some information as to whether the above reaction products were nitrites or nitrates, the lead peroxide was removed from the absorption tube after all the above experiments were completed and extracted three times with 75-cc. portions of a 33 per cent alcohol solution. The extracts were filtered and evaporated to dryness at room temperature by blowing filtered air into the beakers containing them. The successive fractions yielded practically white, crystalline residues, the weights of the fractions being, respectively, I = 150 mg., II = 101 mg., III = 22 mg., a total of 273 mg. Summing up the individual increases in weight of the lead peroxide tube in all the experiments and calculating the amount of lead nitrite which would have been formed according to Equation 4 in the nitric oxide-nitrogen experiments yielded 96.83 mg., while in the nitric oxide-oxygen experiments the amount of lead nitrate, formed according to Equation 5, was calculated and yielded 156.24 mg., a total increase in weight of 253.07 mg. If lead nitrate and not lead nitrite was the product ultimately formed in the nitric oxide-nitrogen experiments, the increase in weight would theoretically be 107.19 mg., making the total 263.43 mg., which agrees fairly well with the 273-mg. increase in weight actually found. This confirms roughly Dennstedt's statement that the weight of product isolated by extraction agrees with the increase in weight of the lead peroxide calculated as lead nitrate.

During evaporation of the solvent the substance extracted undergoes some change, for it was found that the residues were insoluble in the solvent originally used to extract them and were also insoluble in distilled water. When put into suspension, acidified with sulfuric acid, warmed to 40° C., and titrated with 0.1 N potassium permanganate only a few drops of the permanganate were reduced, so that only traces of nitrite could be present. It is, of course, possible that a lead nitrite was formed in the nitric oxide experiments and subse-

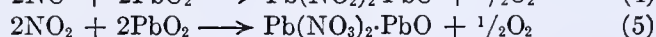


quently oxidized to nitrate during the conditioning of the lead peroxide tube in preparation for the nitrogen peroxide experiments, or during the latter experiments, at which time the nitrite would have been subjected to a temperature of 185°C. in an atmosphere of oxygen; oxidation might also have occurred during the evaporation of the solvent in the air stream. It also appears that during the evaporation of the solvent, the lead nitrate (if that is what was extracted, which is the opinion of Dennstedt) was converted to a basic nitrate which was no longer soluble in the solvent in which it was originally soluble.

### Summary

1. A quantitative study has been made of the reaction between nitrogen peroxide (also nitric oxide) and lead peroxide under conditions similar to those existing in microcombustions.

2. Previous equations given to represent these reactions do not fit the experimental facts. The following equations agree best with the data obtained in the present work:



Equation 4 also agrees with quantitative data obtained by Lindner.

3. The increase in weight of the lead peroxide, calculated as lead nitrate according to Equations 4 and 5, agrees roughly with the weight of product extracted from it by a 33 per cent alcohol solution and confirms Dennstedt's statement to this effect. However, the residue which is weighed does not appear to be lead nitrate, as claimed by Dennstedt, since it is not soluble in the solvent used to extract it, after the original solvent is removed. The presence of nitrite, beyond a trace,

could not be detected in the residue, although it is possible that any nitrite originally formed was oxidized to nitrate before or during attempts at isolation.

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## Identification of Sulfanilamide

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RECENTLY quantitative methods for the colorimetric determination of sulfanilamide in biological media have been reported (8, 12, 13, 17). Since these are diazotization procedures and will not differentiate arylamines, a method involving the use of sodium hypochlorite was suggested (17) to distinguish para-substituted amines from other aromatic amines. None of these methods is entirely specific, and since the drug has been found to possess toxic properties and fatalities have been reported as a result of its administration (1, 2, 7, 14, 15, 19), it was considered essential for toxicological purposes to devise microscopic tests by which the presence of sulfanilamide could be conclusively demonstrated.

It has been pointed out (18) that sulfanilamide is a variant vinyllog of urea, giving an analogous dixanthyl derivative. This reaction is slow, and crystallization does not occur from solutions containing 100 mg. per cent of the drug when treated according to the method of Fosse (6). Like urea, sulfanilamide undergoes a formol condensation in neutral and slightly alkaline media. The product appears to be a polymer of the urea-formaldehyde type. This reaction is applicable to dilute solutions, the condensation of 10 to 15 gamma of sulfanilamide being visible microscopically. Using one drop (0.04 cc.) of sulfanilamide solution (50 mg. per cent) crystals of 1-amino-2, 6-diiodobenzene-4-sulfonamide (16) may be

prepared. Crystals of the picrate may be prepared through hydrochloride formation, using one drop of 30 mg. per cent solution or less.

Fuller (8) isolated sulfanilamide from urine as the highly insoluble mercury salt. Using 0.50 cc. of aqueous sulfanilamide and 0.30 cc. of standard dilute Nessler's reagent, precipitations occurred in 1 to 5 minutes at and above concentrations of 60 mg. per cent. At a concentration of 40 mg. per cent, a turbidity occurred on standing for 12 hours, whereas at lower concentrations the solutions remained clear. Dilute solutions of the drug may be titrated with mercuric nitrate as in the Liebig method (11) for the determination of urea. The precipitation is such that gravimetric methods may be employed, or the precipitate may be dissolved in dilute acid and the sulfanilamide determined colorimetrically by diazotization procedures. (At concentrations of 0.5 to 2.0 mg. per cent, the mercury does not interfere with the color formation.) Microscopically, the crystals obtained are very small, somewhat transparent, and highly flocculated. It was not found possible to single out crystals of clear definition. However, the precipitation of as little as 10 to 15 gamma of sulfanilamide may be observed, preferably in a dark field.

Sulfanilamide forms a silver salt, but it was not found



practicable to reduce this procedure to microscopic proportions. Like other aromatic amines, sulfanilamide is oxidized with the formation of evanescent colors by the action of ammonium persulfate. This color is stabilized somewhat by the presence of silver ions (3). It is deep pink-yellow at 10 but negligible at 1.0 mg. per cent. The color fades within half an hour.

Boiling solutions of the drug with one-tenth of a volume of concentrated nitric acid gave a faint yellow color which became intensified upon the addition of sodium hydroxide to alkalinity. This color is due to a soluble substance which exhibits a nitrolic acid type of tautomerism. It was very intense for solutions containing 100 grams per cent, intense at 10, but negligible at 1 mg. per cent of the drug. Erdmann's reagent gives the same color phenomena, due presumably to the same nitration processes.

Like aniline, sulfanilamide forms a urea derivative when treated according to the method of Davis and Blanchard (4). It was not found practicable to reduce this reaction to microscopic dimensions according to the method of Emich (5). Minute amounts of the crystalline substance treated with a drop of acetic anhydride in the cold on a microscope slide are converted to crystals of the acetylsulfanilamide. However, if 2 drops of acetic anhydride are used and the reaction mixture is boiled over a micro flame, needles of the diacetylsulfanilamide separate in cooling. Two or three milligrams suffice for these tests.

### Experimental

**FORMOL CONDENSATION.** One drop (0.04 cc.) of 100 mg. per cent sulfanilamide solution, 1 drop of 40 per cent formalin, and 1 drop of 10 per cent sodium carbonate were mixed on a microscope slide and the mixture was evaporated to dryness on a water bath. The residue was extracted with 2-drop portions of warm water until free of soluble salts. The product (m. p. 235–240° C. decomposition) appeared as transparent spheres at high magnifications. It was soluble in caustic and warm concentrated hydrochloric acid. The test is sensitive to one drop of 30 mg. per cent solution, or 12 gamma. The product prepared in 0.01 M amounts by the method of Hug (10) appears to be the urea-formaldehyde type, although molecular weight determinations were unsuccessful because of the insolubility of the product. Calculated for  $(C_6H_5O_2SN_2)_x$ : N = 14.29. Found: N = 14.40.

**1-AMINO-2,6-DIODOBENZENE-4-SULFONAMIDE.** One drop of sulfanilamide solution (50 to 100 mg. per cent) and 1 drop of iodine monochloride solution were evaporated to dryness. A drop of water was added to dryness and a second drop of hot water was added, stirred, and drawn off with absorbent filter paper. Alkali-soluble, water- and acid-insoluble needles were obtained (m. p. 265° C. decomposition, 16). Purification was repeated when the crystals were colored, and occasionally it was necessary to evaporate the product with a drop of dilute alcohol to obtain good crystals. The iodine monochloride solution was prepared by adding slowly and with stirring 6.6 grams of sodium iodate to 11.0 grams of potassium iodide in 85 cc. of 6 N hydrochloric acid.

**PICRATE.** One drop of concentrated hydrochloric acid and 1 drop of sulfanilamide solution were evaporated to dryness. The hydrochloride (9, m. p. 235–237° C.) was converted to the picrate by the addition of a small drop of saturated picric acid solution. The test is sensitive to 1 drop of 30 mg. per cent solution: long yellow needles (m. p. 179–180° C.). Calculated for  $C_{12}H_{11}O_9N_3S$ : N = 17.45. Found: N = 17.28, 17.37.

**MERCURY SALT.** To one drop (0.04 cc.) of sulfanilamide solution and 1 drop of mercuric nitrate solution, 1 drop of 10 per cent sodium carbonate was added. A highly flocculated, transparent, white precipitate formed. The particles were extremely small. It was not found possible to single out crystals of good definition. The test is best performed in a dark field or against a black background. Macroscopically the substance has a yellow tint. It dissolves in dilute acids and the sulfanilamide amino group may be diazotized.

The mercuric nitrate reagent was prepared by dissolving a small amount in water with sufficient nitric acid to prevent precipitation upon dilution. It was then diluted until, when mixed with an equal volume of 100 mg. per cent sulfanilamide, it gave a pure white precipitate upon the addition of sodium carbonate (10 per cent). At this dilution, addition of sodium carbonate to

the reagent alone imparted only a slightly yellow tinge to the solution.

**SILVER SALT.** One mole of sulfanilamide (0.400 gram) and 1 mole of silver nitrate were dissolved in 120 cc. of water and 2 drops of concentrated ammonium hydroxide were added. A white precipitation occurred. The reaction mixture was boiled and filtered hot and on cooling white needles separated. The yield was 0.280 gram or 43 per cent. Calculated for  $C_6H_7O_2N_2Ag$ : Ag = 38.70. Found: Ag = 38.28.

**DI-(p-SULFAMIDOPHENYL) UREA.** Treatment of sulfanilamide hydrochloride with urea, according to the method of Davis and Blanchard (4) gave poor yields of the product. The yields were increased slightly upon prolonged treatment, with renewal of urea. The product is soluble in caustic, insoluble in acids, and may be hydrolyzed by hot acids, liberating sulfanilamide: white needles (m. p. 270–271° C. decomposition). Calculated for  $C_{13}H_{14}O_5S_2N_4$ : N = 15.13. Found: N = 15.12, 15.00, 15.12.

**DIACETYSULFANILAMIDE.** A few small crystals of sulfanilamide treated on a microscope slide with a drop of acetic anhydride were observed to change to the acetylsulfanilamide. Washed with ether, the product (16) melted at 214° C. When 2 acetic anhydride were used and the mixture was boiled over a drops of microflame, crystals of the diacetylsulfanilamide separated on cooling. Washed with ether the product, white needles, melted at 240–242° C. with decomposition.

In macroscopic amounts the sulfanilamide was boiled for 10 minutes in an excess of acetic anhydride. The product did not diazotize. Hydrolysis at 100° C. with 2 N hydrochloric acid liberated sulfanilamide. Recrystallized from dilute alcohol (m. p. 244° C. decomposition). Calculated for  $C_{10}H_{12}O_4SN_2$ : N = 10.94. Found: N = 10.64.

### Summary

The reactions of sulfanilamide with formalin, iodine monochloride, picric acid, and various mercuric salts have been reduced to microscopic proportions and by means of these as little as 10 to 40 gamma of sulfanilamide may be identified. Sulfanilamide has been found to undergo a phenol-like reaction with nitric acid. Ammonium persulfate has been observed to produce evanescent colors with the drug, and this color has been stabilized somewhat by the presence of silver ions. Diacetylsulfanilamide and di-(p-sulfamidophenyl)urea have been prepared.

### Acknowledgment

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# An Improved Capillary Clamp

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IN MANY microchemical procedures it frequently becomes necessary to measure the diameter of glass tubing or capillaries—the test tubes of the microchemist—with a high degree of accuracy. To make this measurement, the object is placed vertically in the optical axis of the microscope and the diameter is determined with a previously calibrated micrometer eyepiece. If such measurements are made frequently—in routine analyses or in courses on microtechnic (2, 4, 5)—the use of a special capillary clamp is recommended which facilitates the mounting of the object. Such holders have been described (2, 4, 5); Figure 1 shows an improved design. (This capillary clamp is obtainable from the Arthur H. Thomas Co., Philadelphia, Pa.)

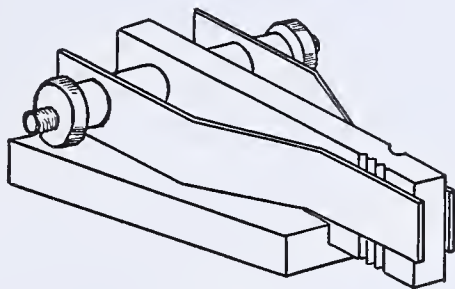


FIGURE 1

The advantages of this inexpensive clamp of nickel-plated brass over previous forms are as follows: The heavy trapezoidal base plate stabilizes the clamp, so that the tendency towards tilting is considerably reduced, even if heavier objects have to be supported, such as Pregl's absorption tubes, in which the dimensions of the capillary endings must be accurately verified (2, p. 227). The dimensions of this base plate are chosen in accordance with the average dimensions of the ordinary rotating microscope stages. The side screws allow a fine adjustment of the pressure exerted by the spring clamps against the capillaries. Objects of different diameters are held safely; the single groove on the back (Figure 1) has a diameter of 2 mm. and serves to clamp tubes of diameters up to 10 mm.; the 3 fine grooves, 0.8 mm. in diameter

and the same distance apart, hold smaller objects of diameters below 2 mm. As the spring exerts only a slight pressure against the horizontal arm, which is 13 mm. high and 4 mm. thick, thin-walled capillaries, 0.3 mm. or less in outside diameter, are not bent, a condition which would interfere with the passage of the light beam, at least in some instances. For extremely fine objects, such as fibers, capillary rods, etc., a thin piece of rubber sheet is placed over the grooves as a cushion. The spring clamps are easily renewed if they lose their elasticity.

The numerous possible applications include: determination of the bore of capillaries used for all qualitative experiments (4, p. 36; 5); observation of the color of liquids in capillaries (coloriscope capillary, 2, p. 226; 4, p. 93; 5); comparison of three colors by means of the three grooves, thus eliminating any doubtful observations in sensitive color tests where the reagent itself has a slight color (blank tests in Feigl's spot tests); standardization of capillary pipets used in Emich's *schlieren* experiments (4, p. 46; 5, p. 40); holding of needle electrodes during the observation of metallic deposits; and control of further manipulations (1; 2, p. 236).

Recently (3), this clamp has rendered excellent service in determining the extremely small bore at the fine tip of weighing capillaries used when liquids of high vapor pressure or high hygroscopicity are to be weighed for quantitative milligram procedures. According to the experience of the author, the bores must be within the range of 0.03 to 0.05 mm. to prevent any evaporation or moisture absorption during the weighing procedure, since these capillaries should not be sealed.

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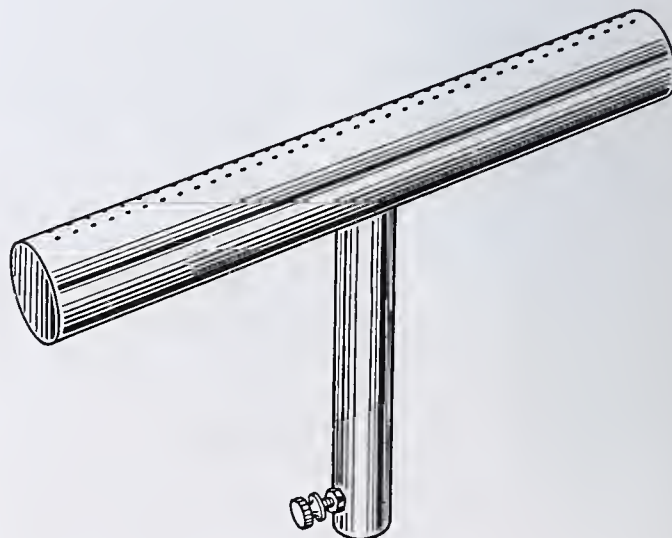
## A "Long Burner" Adapter for Bunsen Burners

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THE adapter pictured here fits over the barrel of a Tirrill or other type of Bunsen burner, and may be used in place of the common "long burner" in the micro and semimicro combustion methods of ultimate organic analysis and for bending glass tubing of large diameter. It is inexpensive and easily regulated as to size of flame and height. It will burn natural gas and water gas satisfactorily.

It consists of a brass pipe of standard 0.094-inch stock, 7 inches long and 1 inch in outside diameter. The ends of the pipe are closed flush by means of two brazed caps. Two rows of thirty-six holes 0.056 inch in diameter and 0.19 inch apart are drilled along the top of the burner piece.

The barrel, of 0.094-inch stock is 4.5 inches long and about 0.5 inch in inside diameter. It is threaded and soldered into the bottom of the burner piece at the center. A set screw near the bottom of the barrel allows adjustment of the height.



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# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Analysis of Caramel Color

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**Sixteen million pounds of caramel color—burnt sugar coloring—are produced annually in the United States for use in the beverage, food, and pharmaceutical industries. No uniform methods for the analysis of caramel color have ever been published, and the author presents this paper on analytical procedure which will evaluate a caramel color not only for type but also for quality.**

CARAMEL color, or burnt sugar coloring, is used extensively in carbonated beverages, distilled liquors, wines, pharmaceuticals, extracts, bakery products, candy, soups, and baked beans. Figures on the amount manufactured are not available, as many concerns make their own coloring. According to the 1929 census of the Department of Commerce, fifty-three establishments were producing 1,450,000 gallons of caramel. More recent comparable data are not available but it is believed that there are fewer producers of caramel today. The 1935 census gives a production of 1,550,000 gallons and an estimate of production today would be in excess of 1,600,000 gallons. This increase is attributable to increase in amount of carbonated beverages consumed.

Very little has been published about either the manufacturing or testing of caramel color. Probably the best article is that of Salamon and Goldie, published in 1900 (6). These authors presented data on its manufacture, and their tests in modified form are largely in use today. Brewers' caramel has received more attention than caramel for carbonated beverages, although the latter requires a caramel of more specialized characteristics.

The manufacture, with few exceptions, is carried on by "burners" who employ rule-of-thumb methods, so that there is considerable variation in the finished product. There are many methods of evaluating caramel, each manufacturer having his own tests for standardization of his product. Consumers, for the most part, are comparatively small users who do not test the caramel, but once they have a satisfactory source of supply will change only under the most unusual circumstances. Large users of caramel, with well-equipped laboratories, have their own tests, peculiar to their product. Their experience with various makes of caramel, in many instances, has been as unsatisfactory as that of the small user, so that they are equally conservative with regard to changing their source of supply.

The trouble with caramel color is probably due to the fact that the conditions which a caramel must meet in specialized uses, such as carbonated beverages and pharmaceuticals, involve several characteristics which are equally important. Too often one is overemphasized or overlooked.

The laboratory has offered little aid to the user who would resort to a chemical analysis. Probably the greatest difficulty lies in the multitude of methods in use, with the consequent lack of uniformity in evaluation by different laboratories. In addition, most laboratory analyses are not sufficiently comprehensive to cover caramel in general, but are built around a specific use. Even the simple test of tinctorial or coloring power of a caramel varies between laboratories, because of failure to follow a uniform method of measurement.

This paper is presented in the interests of a standardized procedure for the analysis of caramel color. The tests include not only those that have been developed in the author's laboratory but those of consumers and manufacturers, modified in some instances to fit the usual laboratory practice and to obtain a more general application. The tests given will evaluate a caramel both as to quality and type.

### Caramel Types

Caramel is used in a wide range of products and is manufactured in a number of types, each designed for a specific purpose. These include types for carbonated beverage manufacturers (including acidproof, nonacidproof, and foaming), brewers, distillers, bakers, and confectioners. Carbonated beverages, extracts, and distilled liquors require the highest quality of caramel. Caramel satisfactory for bakery and ice cream use may be entirely unsuitable for beverage use. True beer caramels cannot be used for carbonated beverages, although they serve satisfactorily in the bakery, in ice cream, and in candy. Carbonated beverage caramels, as a rule, cannot be used for hard candy because of their high acid content, which would cause inversion in the candy.

Various types of caramel may be used in carbonated beverages. Thus, ginger ales and cola beverages require an acid-fast and tannin-resistant caramel. Root beer and cream soda do not require an acid-fast caramel, but one with good tannin resistance. If the root beer is a true root extract, the tannin requirements are greater than if synthetic flavors are used. However, an acid-fast caramel with high tannin resistance can be used in all carbonated beverages. Thus, any consideration of caramel quality must take into consideration the service to which the caramel is put. Although an apparently poor caramel may give the best of service in an isolated instance, it is far safer to demand a high laboratory



rating, or a caramel designed for exacting service, than to use a lower quality, where the margin of safety may be so small that a slight alteration in ingredients may cause precipitation of the caramel.

### Analysis of Caramel

Laboratory testing of caramel is based on a series of tests under specified conditions which bear a relationship to actual conditions. This series of tests will readily differentiate caramel as to grade and quality, but the individual must determine the grade suitable to his product and the variations in quality that his product can stand. This includes a consideration of shelf life. Thus, a cola or ginger ale dispensed at fountains and immediately consumed does not require the same acid-fastness in a caramel as the same beverage when bottled, where the shelf life may be over three months.

The following solutions are used in the tests:

A. Caramel Solution, 1 per cent. Dissolve 10.000 grams of caramel color in distilled water and make to 1 liter.

B. Acid Tannin Solution. Dissolve 0.1 gram of tannic acid U. S. P. and 15 grams of citric acid U. S. P. in 100 ml. of distilled water. Refilter until clear. This solution deteriorates rapidly and must be prepared daily.

C. Tannic Acid Solution. Dissolve 1 gram of tannic acid U. S. P. in 100 ml. of distilled water. Refilter until clear. Make up solution daily.

D. Alcohol Tannin. Dissolve 0.5 gram of tannic acid U. S. P. in 100 ml. of 50 per cent alcohol by volume.

E. Alcohol Solution, 50 per cent by volume.

F. Alcohol Solution, 55 per cent by volume.

G. Alcohol Solution, 60 per cent by volume.

H. Alcohol Solution, 65 per cent by volume.

For recording observations, the following notations may be employed:

A. Brilliant at end of 24 hours.

B. Slight haze at end of 24 hours.

C. Slight precipitate at end of 24 hours.

D. Medium precipitate at end of 24 hours.

E. Heavy precipitate at end of 24 hours.

F. Immediate precipitate, in case of acid test during the boiling period.

The 1 per cent stock caramel solution should be examined by transmitted and reflected light, recording observations as (1) brilliant, (2) hazy, or (3) opalescent.

After filtering through a 15-cm. (6-inch) filter paper, observations are recorded as (1) clean, (2) suspended matter, or (3) char.

### General Tests

**SPECIFIC GRAVITY.** The specific gravity of commercial caramels varies widely, ranging from 34° to 42° Bé., with an average of approximately 38.0° Bé. A uniform gravity is especially important in carbonated beverage caramels, because when large quantities of caramel are used, as in root beer concentrate, variations in Baumé of the caramel will affect the final gravity of the concentrate.

High gravities generally result from the burner's failure to produce the necessary amount of color in the burning process. Thus, in adding water to "burnt" mass, he cuts back to the desired tinctorial power, without regard for gravity. Such caramels drain with difficulty and very slowly from the containers. Low gravities are generally the result of an attempt to obtain a freer flowing caramel. With a lower gravity, more color must be produced in the burning process, so that such a caramel must be examined carefully for overburning with resultant failure in quality.

Immerse a hydrometer standardized at 15.56° C. (60° F.) in air-free caramel at 15.56° C. (60° F.) and obtain the reading. If a temperature correction is necessary, employ the arbitrary correction of 2.2224° C. (4° F.) equals 0.1° Bé.

When the sample of caramel is small, particularly if the gravity is high or the viscosity great, it is best to use a Hubbard-Carmick specific gravity bottle, which is designed primarily for asphalt.

**TINCTORIAL POWER.** Probably no other part of a caramel analysis has varied more than the measurement of tinctorial power. As defined by Salamon and Goldie (6), the tinctorial power is the Lovibond reading obtained on a caramel solution, made by dissolving 1 gram of color in 1 liter of distilled water, in a 2.5-cm. (1-inch) cell. The trouble may generally be attributed to three causes:

**Standard Glasses.** The usual Lovibond glasses employed in the measurement of caramel color are the Caramel Series No. 52. These slides were designed for the measurement of color in beer (4) and may or may not match the color produced by commercial caramel color. As a rule, beer caramels match very well; distillers' caramels do not, as they contain more red than the No. 52 series. The carbonated beverage caramels lie between. In reading a distillers' or carbonated beverage caramel with No. 52 slides only, the tendency is to employ too many slides in order to secure a match, resulting in too high a tinctorial power. This can be overcome by adding 0.1 to 0.4 red to the No. 52 series.

**Light Source.** The original Lovibond light for standardization was that reflected from a fog bank by the early morning sun across the meadow from the Lovibond brewery. This is a soft diffused light and may be matched for purposes of standardization by picking a time when similar light conditions exist. The source in the laboratory is the electric light, and the common tendency of chemists is to employ too much light, resulting in readings that are too low. A good source can be obtained by passing the light of a 50-watt lamp through a daylight glass against white crepe filter paper at a 45° angle from the Lovibond cells. Once a source of light has been established, it should be adhered to.

**Cells.** The definition of tinctorial power calls for measurement in a 2.5-cm. (1-inch) cell. Many laboratories do not have an inch cell, but do possess 0.63- and 1.25-cm. (0.25- and 0.5-inch) cells. In the latter case, the reading on a 0.1 per cent solution is multiplied by two, or the reading on a 0.2 per cent solution is made and called the tinctorial power. This leads to erroneous results, as the Lovibond reading under these conditions is not proportional for all caramel colors and may vary as much as 10 per cent from results obtained by a reading on a 2.5-cm. (1-inch) cell.

The British Drug House modification of the Lovibond tintometer is an improvement over the older form. Carbonated beverage caramels require the addition of the red



FIGURE 1. DUBOSCQ TYPE OF TINTOMETER



series (200) in addition to the No. 52 Caramel Series and it is advisable to introduce about 0.2 red at the start, adding the caramel slides until an approximate match has been obtained, after which the effect of an additional 0.1 red on the match may be studied.

Other types of tintometers are in use. Figure 1 shows a Duboscq type in which a fixed glass standard is used. The degree of variation is measured on the drum, according to the degree of immersion of the plunger above or below the depth of definite solution, matching the glass standard, which is given the arbitrary rating of 100. Figure 2 shows a newer modification of the Duboscq. Lovibond slides are contained in the metal disks as follows:

Caramel Series 52	30		20		15		10	
	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0
	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2
Red Series 200	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2

This comparator has the advantage that the maximum number of slides which can be used is four, which is desirable with the Lovibond system. In addition, the amount of light passing through the caramel may be altered by the reflector, thus compensating for the brilliance often found in some caramels and also for the differences in light absorption by different combinations of slides. This may also be done in the British Drug House tintometer by the addition of neutral slides, but it has been the author's experience that the employment of these neutral tints complicates rather than aids the matching.

To determine the tinctorial power, dilute 50.0 ml. of stock caramel solution A to 500 ml., and read the color in a 2.5-cm. (1-inch) cell, using Lovibond glasses Series 52. Add 0.1 to 0.4 red if necessary to secure an exact match.

**pH.** The pH of a caramel gives an index of its quality and may be measured by either glass or quinhydrone electrodes. The readings by the former are usually slightly lower. If the quinhydrone electrode is employed, an excessive amount of quinhydrone must be used to prevent drifting and the gold electrode must be kept clean. An undiluted caramel with a pH higher than 6.0 will mold. High pH also indicates an incomplete "burn" or excessive amounts of alkali, both of which mean that the caramel will increase in tinctorial power on aging. Caramels have been examined with pH as high as 9.

Carbonated beverage caramels, undiluted, should run from 2.5 to 3.3 (glass electrode). Caramels with pH less than 2.5 are likely to resinify, and have been known to become rubberlike or even turn to a solid within two months.

The pH of a 15 per cent solution, intended primarily for beer caramels, should run from 4.5 to 5.0 under these conditions, comparable to the fermentation pH. Caramels which give higher or lower pH under these conditions when added to the fermenting wort are said to alter the pH sufficiently to change the flavor of the resulting beer.

The pH of 1 per cent solution in a carbonated beverage caramel should run approximately 3.5. pH lower than 3.3 indicates a caramel with excessive residual acidity.

Obtain the pH of a caramel by means of a glass or quinhydrone electrode.

To determine the pH of a 15 per cent solution proceed in the same way on a solution of caramel made by dissolving 15 grams of caramel and making to 100 ml.

To determine the pH of a 1 per cent solution, take 5 ml. of the above solution, add 70 ml. of distilled water, mix thoroughly, and obtain the pH.

**VISCOSITY.** Relative viscosity is important with reference to the speed with which a caramel resinifies or ages. Caramels with excessive relative viscosity are usually overburnt and lack acid-fastness.

The relative viscosity can easily be determined by using a 50-ml. Mohr buret, filling with caramel at a definite temperature—i. e., 29.44° C. (85° F.)—and collecting 40 ml. in a graduated cylinder.

**ASH.** The ash normally bears no relationship to quality. However, in recent years the hydrol from refined corn-sugar processing has been used for caramel, which increases the ash content, depending upon the amount used, to as high as 8 per cent. Caramels with an ash content greater than 3 per cent, if intended for use in carbonated beverages, should be examined closely for the effect of ash on flavor.

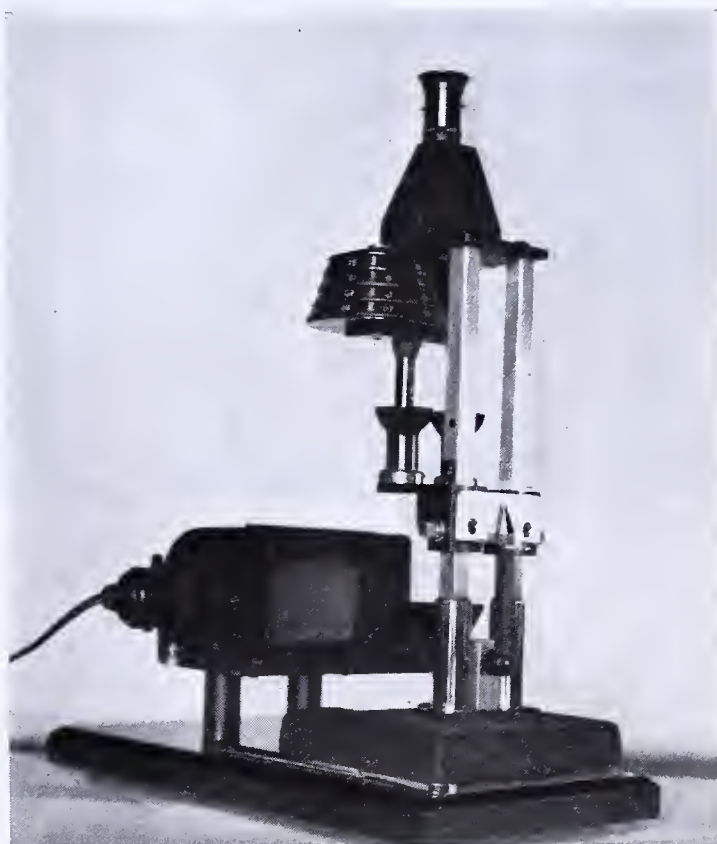


FIGURE 2. MODIFICATION OF DUBOSCQ TINTOMETER

**IRON.** Iron in a caramel will often run to excessive limits, entering through the burning equipment, which is often made of mild steel. Only a few manufacturers employ glass-lined or stainless steel equipment because of the cost involved. Samples of caramel have been examined which have contained 2000 p. p. m. of iron. The effect of this iron on the flavor of a pharmaceutical extract or carbonated beverage can well be imagined.

The ash is dissolved in acid and the iron content measured colorimetrically (1).

### Specific Tests for Carbonated Beverage, Pharmaceutical, and Distillers' Caramel

**ACID TEST.** This test, which is particularly important in caramel color used in cola and ginger ale beverages, has been found adequate by an old manufacturer in evaluating caramel color.

Dilute 50.0 ml. of stock caramel solution A to 250 ml. with distilled water, add 7 ml. of concentrated hydrochloric acid (sp. gr. 1.18), cap, and boil gently for 5 minutes. Remove from flame and note whether precipitation has developed. Set aside and record observation 24 hours later.

If the color is satisfactory, a measure of residual acid-fastness may be obtained by repeating the above test, boiling for 30 minutes instead of 5 minutes. Water must be added at intervals to maintain a constant volume.



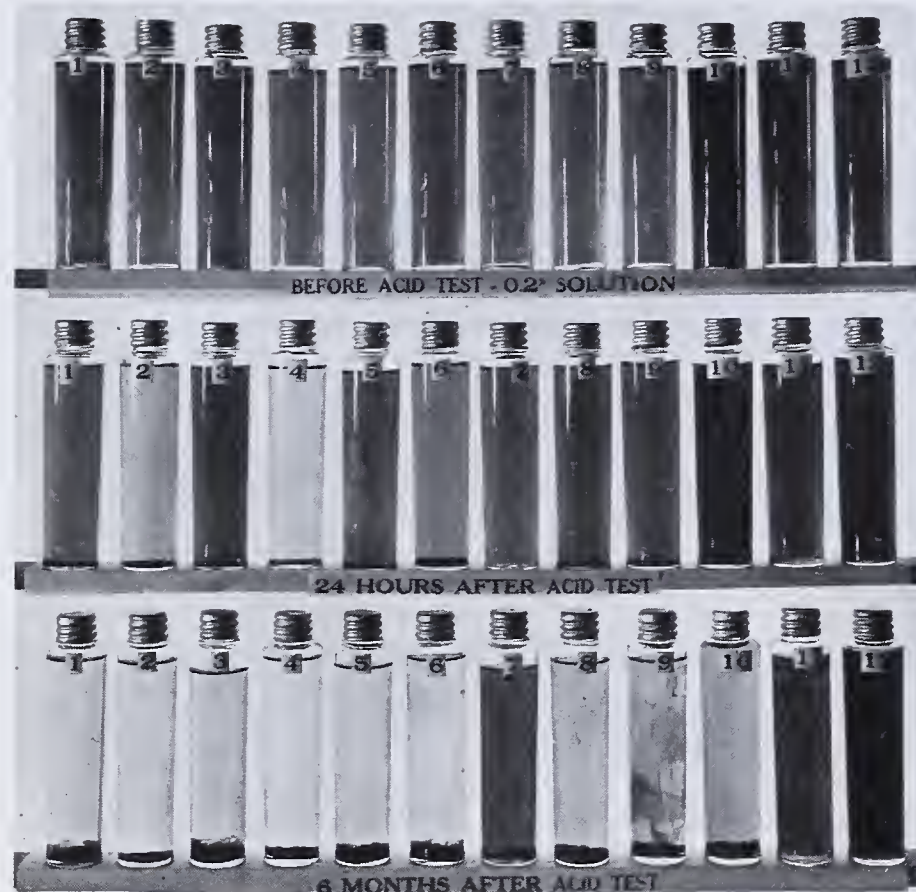


FIGURE 3. ACID TEST FOR CARBONATED BEVERAGE CARMELS

**NEUTRAL TANNIN TEST.** These tests are a measure of caramel's resistance to flocculation by extractives that occur in the various carbonated beverages and pharmaceutical extracts.

1. To 80 ml. of distilled water add 10 ml. of stock caramel solution A, then 10 ml. of stock tannin acid solution C, and mix thoroughly. If clear, set aside for 24 hours and record observations.

2. To 50 ml. of distilled water add 25 ml. of caramel solution, and then 25 ml. of tannic acid solution, and mix thoroughly. If clear, set aside for 24 hours and record observations.

3. To 13 ml. of caramel solution, add 12 ml. of tannic acid solution, and mix thoroughly. If clear, set aside for 24 hours and record observations.

**ACID-TANNIN TEST.** This is a combined acid and tannin test. To 75 ml. of acidulated tannic acid solution B, add 5 ml. of stock caramel solution A and 20 ml. of distilled water, and mix thoroughly. If clear, record observations at end of 24 hours.

**ALCOHOL TESTS.** Dissolve 1 gram of caramel in 100 ml. each of 50, 55, 60, and 65 per cent alcohol by volume. Mix thoroughly and record observations at end of 24 hours.

**WHISKY TEST.** Color 50 ml. of test solution D a distinct brown (the color of a 0.2 per cent solution) and observe 24 hours later.

**FERMENTATION TEST.** Some beverage manufacturers depend upon the residual acidity of a caramel color to preserve their extracts. The residual acids in a caramel are a combination of those resulting from the catalyst used—i. e., ammonium sulfate—and those produced in the burning process—i. e., acetic acid. Titratable acidity data obtained on different makes of caramel are not comparable, since the methods of burning and catalysts used differ. For this reason, pH data are better. As a rule, a pH of at least 3.0 is required to assure no fermentation, but this cannot be taken as a final criterion, as there is considerable variation in the buffering power of caramels, depending on the type of catalyst employed and the method of burning. A measure of the effectiveness of the residual acidity is the fermentation test.

To 10 ml. of color add 20 ml. of distilled water, mix thoroughly, add 0.5 gram of compressed yeast, and stir until completely suspended. Pour into a fermentation tube and invert for 15 minutes or until all the air has been eliminated. Place tube in position, plug with cotton, and set aside for 48 hours at 26.67° to 32.22° C. (80° to 90° F.). Record the percentage volume of gas produced.

**FOAM TEST.** Caramels for carbonated beverage use are of foaming and nonfoaming types. The former are used for root beer and the latter for cola and ginger ale beverages. Foaming caramels are used in "mug" root beer, where a large stein is drawn, containing a large head of foam. Caramels can be burnt to have foaming qualities, eliminating any necessity for the addition of saponin or other similar foaming agents. Under the test outlined below, a caramel designed for cola or ginger ale will give a head of foam lasting from 3 to 6 minutes, with bubbles that are large and break quickly. A foaming caramel will give a head of fine bubbles lasting from 30 minutes to 2 hours.

Dissolve 10 grams of caramel in distilled water, make to 100 ml., run into a 250-ml. glass-stoppered cylinder, and shake for 2 minutes. Loosen the stopper and place in a water bath at 37.78° C. (100° F.). Observe the time for the head of foam to fall to the liquor surface.

**COMPATIBILITY.** One of the most serious difficulties in the use of caramel for carbonated beverages occurs when caramel is added to a sirup or extract already containing caramel, or where two makes of caramel are used in the same plant. The weaker or inferior caramel will often precipitate out.

**Filter Paper Test.** Run 1 or 2 ml. of a 0.2 per cent solution of caramel onto a large sheet of filter paper. The color from a satisfactory caramel will follow the water. The color from an inferior caramel will collect in a spot in the center, and the water will proceed to form a larger circular area. Such a caramel is invariably noncompatible.

**Solution Test.** Dilute 50 ml. of solution A of each caramel to 250 ml. and proceed as follows:

Caramel A, ml.	2	4	6	etc.	14	16	18
Caramel B, ml.	18	16	14	etc.	6	4	2
Distilled water, ml.	80	80	80	etc.	80	80	80

TABLE I. PHYSICAL EXAMINATION

Solution	Brilliant	Brilliant	Hazy
Retained on filter paper	Clean	Clean	Clean
Baumé	38.1°	39.1°	37.5°
Tinctorial power	22.1	19.5	21.0
Acid test, 5 minutes	A	A	F
Acid test, 30 minutes	D	E	F
Neutral tannin 1	A	A	A
Neutral tannin 2	A	A	A
Neutral tannin 3	A	B	F
Acid tannin	A	A	E
Alcohol, 50%	A	A	A
Alcohol, 55%	A	B	C
Alcohol, 60%	B	E	F
Whisky test	A	A	B
Foam test, minutes	7	6	20
Hops test, %	100	100	100
Fermentation test	None	None	Trace
Compatibility:			
Filter paper test	OK	OK	OK
Solution test	OK	OK	OK
pH	3.0	2.9	3.3
pH, 15%	3.0	2.9	3.3
pH, 1%	3.5	3.6	3.7
Viscosity, 29.44° C. (85° F.):			
water = 1	20.	a	65.
Iron, p. p. m.	<10.	30.	230.

a Too thick to measure.





FIGURE 4. SHIPPING FLOOR OF CARAMEL DEPARTMENT

Pour into oil sample bottles, pasteurize, and seal. Set aside for 24 hours and record observations.

### Tests Specific for Brewers' Caramel

The requirements for a caramel in beer are entirely different from those for a carbonated beverage, pharmaceutical, or distillers' caramel. Brewers' caramels are sometimes burnt from malt sirup and designated malt caramels; more often they are burnt from mixtures of malt and corn-sugar sirup. Excellent brewers' caramels may be burnt entirely from corn sugar, with the proper burning formula, and add only color to the beer. Those from malt contribute flavor in addition.

The pH of the caramel, particularly after dilution, is important (2, 3, 4, 5). The caramel must not fade or bleach when boiled with hops and it must be chill-proof—i. e., there must be no sedimentation or fading when the beer is chilled, either in brewery storage or previous to its consumption.

**Hops Test.** Run 200.0 ml. of the stock caramel solution into a 500-ml. flask, add 1.0 gram of dried hops (pale green in color), cover the flask with a small beaker, and boil gently for 15 minutes. Cool and filter through a Gooch crucible or Hirsch funnel, prepared with a layer of asbestos, over which is a layer of Filter-Cel. Wash and make the filtrate to 1 liter. Compare with a control made from 50.0 ml. of the stock caramel solution diluted with distilled water to 250.0 ml.

Record the percentage of the color remaining after boiling with hops, employing the respective Lovibond readings to determine the loss, if any.

**CHILL-PROOF TEST.** Chill two bottles of beer, to which color is to be added, from 0° to 4° C. (32° to 39° F.) by means of an ice bath. For control purposes, remove the crown cap from one and immediately recap. Remove the crown cap from the other bottle, add 1 gram of color, and recap. Agitate the beer until the caramel is dissolved. Place both bottles in an ice bath or refrigerator for 24 hours and examine for appearance of haze or sediment. Usually 24 hours will suffice for this test.

### Summary

To illustrate the type of data obtained by this procedure, three typical analyses of commercial caramel colors sold for carbonated beverages are given in Table I.

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## Counting Drops with the Photoelectric Relay

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THE photoelectric relay may be used to count drops of transparent liquids. By suitable regulation of the cross section of the light beam used, drops forming in the beam will reflect and refract sufficient light to act like opaque objects. This will cause the photoelectric cell to produce electrical impulses which may be used to count the number of drops for an interval of time or to regulate the rate of dropping.

In the apparatus used by the author, the beam of light is modified by vertical slits 0.5 cm. wide by 1 cm. long. The beam runs horizontally across the source of drops and directly to the photoelectric cell, being interrupted as the drop forms and returning to normal after it has fallen. With the potentiometer set at 226° and an electric relay counter operating on 18.6 volts direct current, it was found possible to count drops up to 478 per minute. Faster counts are difficult because of the tendency of the drops to lose their identity and form a continuous stream.

Drops may be enclosed by transparent material, so that they are neither mechanically damaged nor chemically contaminated.

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# Sulfuric Acid Analysis of Gaseous Olefins

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Principles and limitations governing the selection of conditions for determination of gaseous olefins by absorption in sulfuric acid are presented briefly. Data indicating the influence of the following previously uninvestigated factors upon analytical results are given: (1) reversibility of absorption; (2) solubility of gaseous paraffins in sulfuric acid; (3) increase in solubility of hydrocarbons because of acid-soluble ab-

sorption products; (4) solubility of hydrocarbons in precipitated polymer products; and (5) liberation of unabsorbable gas by overstrong absorbents, including those containing silver sulfate. Suitable apparatus and technic for overcoming these effects are described. Within its natural limits of applicability, the improved method gives, for samples of all possible olefin concentrations, rapid and reliable results.

**S**YSTEMATIC selection of analytical conditions in accordance with the principles and the limitations discussed in this paper makes the determination of gaseous olefins by absorption in sulfuric acid quantitatively accurate.

## Principles

**RELATIVE RATES OF ABSORPTION.** Figure 1, based primarily on the work of Dobryanski (6), who made the first of several recent studies of the absorption of gaseous olefins by sulfuric acid (2, 3, 5, 11), indicates the relationship between acid concentration and rate of absorption. Dobryanski passed all of a 100-cc. sample of olefin from a gas buret into a cylindrical absorption pipet having no contact tubes. After permitting the acid on the pipet wall to drain for 5 to 10 minutes, he returned about 50 cc. to the buret. Then, after closing a special stopcock in the U-connection leading to the acid-expansion chamber, thereby preventing disturbance of the acid surface, which had a constant area of about 19.9 sq. cm., he followed the absorption by direct buret readings. For each particular combination of unsaturated gas and acid

concentration, the rate of absorption was constant. The observed constant rates of absorption are plotted against acid concentration in Figure 1.

Dobryanski recommended 63 to 64 per cent sulfuric acid for absorbing isobutylene; 83 to 84 per cent acid for propylene, butadiene, and *n*-butenes; and 100 to 102 per cent acid for ethylene. Figure 1 indicates that 63 to 64 per cent acid absorbs isobutylene about 500 times as readily as propylene, and that 83 to 84 per cent acid absorbs propylene about 500 times as readily as ethylene. Contact of a gas sample successively with acid of these strengths thus removes in turn isobutylene, propylene, and ethylene.

*n*-Butenes are absorbed together with propylene because their rate of absorption averages only about twice that of propylene (5, 6, 11). Separation can be effected readily by a preliminary fractional distillation into three-carbon and four-carbon fractions which then are analyzed separately by sulfuric acid absorption.

The diolefin butadiene, if present, is absorbed, for the most part, with the *n*-butenes. Its presence is indicated qualita-

tively by an intense yellow coloration of the acid. Allene appears to be absorbed at a rate similar to that for butadiene (8).

If five-carbon vapors are present, isoprene and tertiary amylenes (trimethyl ethylene and unsymmetrical methyl ethyl ethylene) are absorbed with isobutylene; *n*-amylenes (pentene-1 and pentene-2) and isopropyl ethylene are absorbed with propylene and *n*-butenes (4, 10). For separation from propylene and butylenes, fractional distillation and dilution with an inert gas, followed by sulfuric acid absorption, can be used (4).

**LOGARITHMIC VARIATION OF ABSORPTION RATE WITH ACID CONCENTRATION.** Since the rate of absorption, as is indicated by the straight curves of Figure 1, increases logarithmically with increase in

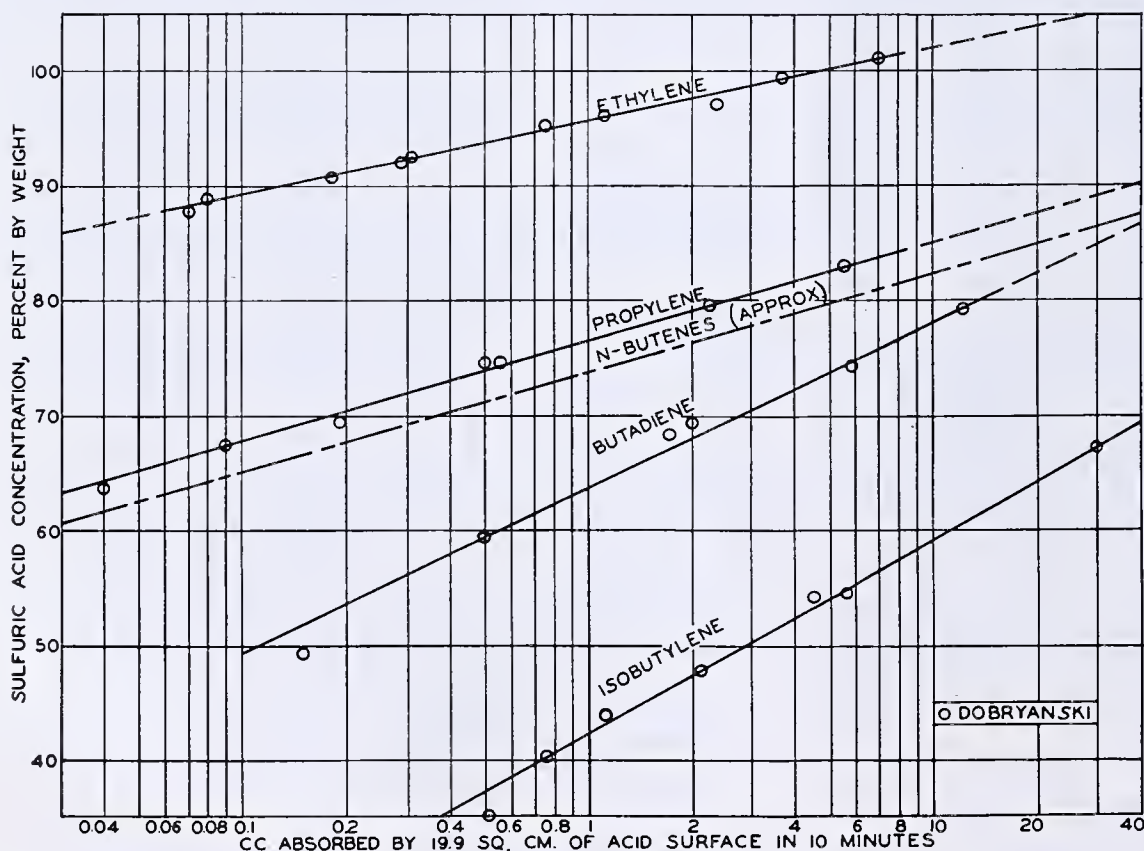


FIGURE 1. ABSORPTION OF UNSATURATED GASES BY SULFURIC ACID



concentration of sulfuric acid, use of the strongest concentration consistent with reliable results greatly shortens the time required for an analysis.

ABSORPTION RATE PROPORTIONAL TO ACID SURFACE. The rate of absorption is independent of the volume of the acid but is directly proportional to its surface area (3, 5).

ABSORPTION RATE PROPORTIONAL TO PARTIAL PRESSURE OF OLEFIN. Since the rate of absorption is proportional to the partial pressure of the olefin (3, 5), the end of the absorption is approached slowly.

Limitations

INCOMPLETE SPECIFICITY OF SULFURIC ACID. Because a small amount of propylene and *n*-butenes can be absorbed with isobutylene and a little ethylene can be absorbed with propylene and *n*-butenes, corrections for incomplete specificity of absorbents must be made. The usual method of making corrections is to continue the absorption with one body of absorbent until a small constant absorption per pass is obtained and to multiply this by the number of passes (8-11). Changes effected by the absorption—in the composition of the gas and in the composition and the effective surface area of the absorbent—and multiplication of small errors by the large number of passes required for complete absorption, especially for high olefin contents, make this method, if unmodified, uncertain and subject to large errors.

REVERSIBILITY OF ABSORPTION. Although under gas-analytical conditions the absorptions of ethylene and of propylene are so nearly complete as to be justifiably regarded as being irreversible, those of the butylenes—probably also of the amylenes—are distinctly reversible. Unless more than one portion of acid is used, up to more than 1 cc. of butylene remains unabsorbed.

PHYSICAL SOLUTION OF PARAFFINS IN SULFURIC ACID. Published data on the solubility of gaseous paraffins in sulfuric acid appear to be limited to the following for methane at 20° C. and one atmosphere (1):

Per cent H <sub>2</sub> SO <sub>4</sub>	0.0	35.9	61.7	95.6
Cc. MeH per cc. acid	0.0350	0.0169	0.0131	0.0308

Table I presents approximate values obtained at about 25° C. for the physical solubility of *n*-butane in sulfuric acid. Three or four 30-second passes of 90 to 100 cc. of the gas were made into the pipet described below, which contained about 2 cc. of acid. The absorption was usually complete after two passes; two-thirds of it occurred in the first pass. After the residual volume was read, the acid above the mercury in the pipet was replaced by a fresh 1.0-cc. portion. This procedure was repeated until a total decrease sufficiently large to be measured by the buret was obtained. Presence of up to 1.50 per cent silver sulfate in 96 per cent acid had no effect.

TABLE I. PHYSICAL SOLUBILITY OF *n*-BUTANE IN SULFURIC ACID SOLUTIONS

H <sub>2</sub> SO <sub>4</sub> %	Solubility, Cc. <i>n</i> -BuH Cc. Acid	H <sub>2</sub> SO <sub>4</sub> %	Solubility, Cc. <i>n</i> -BuH Cc. Acid
60.6	0.001	89.3	0.015
64.7	0.004	91.0	0.036
69.3	0.004	92.5	0.070
77.5	0.010	96.0	0.150
80.7	0.012	99.7	0.30
87.3	0.012	102.0 <sup>a</sup>	0.40
88.5	0.012	104.0 <sup>b</sup>	0.40

<sup>a</sup> 102.0% H<sub>2</sub>SO<sub>4</sub> = 100.0% H<sub>2</sub>SO<sub>4</sub> containing 2.0% free SO<sub>3</sub> by weight.  
<sup>b</sup> 104.0% H<sub>2</sub>SO<sub>4</sub> = 100.0% H<sub>2</sub>SO<sub>4</sub> containing 4.0% free SO<sub>3</sub> by weight.

The data indicate that the error due to solubility of paraffin gases in 1-cc. portions of sulfuric acid of concentrations below

TABLE II. INFLUENCE OF PRESENCE OF DISSOLVED PRODUCTS ON OLEFIN DETERMINATIONS

H <sub>2</sub> SO <sub>4</sub> %	Gases <sup>a</sup> Taken Cc.	1-Cc. Acid Por- tions	30- Sec. Passes <sup>b</sup>	Max. Absorbed per Portion	Olefin %	Error %
99.7	E, 49.60; N <sub>2</sub> , 50.10	1	20	49.50	99.8	...
99.7	E, 57.00; N <sub>2</sub> , 50.20	1	28	106.35 <sup>c</sup>	99.8	...
99.7	E, 79.70; <i>n</i> -BuH, 19.80	1	32	80.00	100.4	+0.6
91.0	P, 79.45; N <sub>2</sub> , 20.10	1	6	78.40	97.4	...
91.0	P, 49.80; <i>n</i> -BuH, 50.00	4	6	42.55	97.8	+0.4
88.5	P, 49.60; N <sub>2</sub> , 49.90	4	8	24.85	97.4	...
88.5	P, 80.15; N <sub>2</sub> , 19.70	6	12	32.85	97.4	...
88.5	P, 80.20; <i>n</i> -BuH, 19.80	5	16	34.35	97.6	+0.2
88.5	P, 49.90; <i>n</i> -BuH, 49.75	5	10	23.25	97.5	+0.1
84.0	P, 50.10; N <sub>2</sub> , 49.70	1	16	48.75	97.4	...
84.0	P, 50.10; <i>n</i> -BuH, 49.60	1	16	48.85	97.5	+0.1
79.9	B-1, 49.50; N <sub>2</sub> , 49.50	9	48	11.90	99.6	...
79.9	B-1, 49.40; <i>n</i> -BuH, 50.20	9	48	13.50	99.7	+0.1
84.0	B-2, 49.60; N <sub>2</sub> , 49.55	4	16	47.90	99.8	...
79.9	B-2, 49.50; <i>n</i> -BuH, 50.25	11	47	14.60	100.0	+0.2
70.2	i-B, 50.40; N <sub>2</sub> , 50.35	8	24	26.95	99.6	...
70.2	i-B, 50.00; <i>n</i> -BuH, 49.75	5	24	50.50	99.9	+0.3
70.2	i-B, 50.30; <i>n</i> -BuH, 49.50	8	24	25.45	99.6	0.0
64.7	i-B, 49.05; N <sub>2</sub> , 49.90	8	28	25.40	99.6	...
64.7	i-B, 79.50; N <sub>2</sub> , 19.90	8	28	22.80	99.6	...
64.7	i-B, 49.50; <i>n</i> -BuH, 49.80	7	36	48.55	99.6	0.0
64.7	i-B, 80.15; <i>n</i> -BuH, 19.70	10	32	26.15	99.6	0.0
64.7	i-B, 48.90; <i>n</i> -BuH, 49.65	9	28	13.80	99.6	0.0

<sup>a</sup> E = 99.8% ethylene; P = 97.4% propylene; B-1 = 99.6% butene-1; B-2 = 99.8% butene-2; i-B = 99.6% isobutylene.  
<sup>b</sup> The sample was kept in the pipet for 30 seconds at each pass, exclusive of inflow and outflow (5 to 7 seconds each).  
<sup>c</sup> The same portion of acid was used as in the preceding analysis.

TABLE III. INFLUENCE OF PRESENCE OF UNDISSOLVED POLYMER ON BUTYLENE DETERMINATIONS

H <sub>2</sub> SO <sub>4</sub> %	Gases <sup>a</sup> Taken Cc.	1-Cc. Acid Por- tions	30- Sec. Passes	Max. Ab- sorbed per Portion	Olefin %	Error %
88.5	B-1, 50.30; N <sub>2</sub> , 50.15	5	12	34.35	99.6	...
79.9	B-1, 49.50; N <sub>2</sub> , 49.45	9	48	11.90	99.6	...
88.5	B-1, 49.95; <i>n</i> -BuH, 49.90	1	12 <sup>b</sup>	51.20	102.5	+2.9
88.5	B-1, 50.55; <i>n</i> -BuH, 49.30	6	16	34.70	100.8	+1.2
84.0	B-2, 49.60; N <sub>2</sub> , 49.55	5	20	47.90	99.8	...
89.3	B-2, 48.40; <i>n</i> -BuH, 48.55	4	7	45.45	102.2	+2.4
88.5	B-2, 50.35; <i>n</i> -BuH, 49.50	1	12 <sup>b</sup>	52.05	103.4	+3.6
86.0	B-2, 49.55; <i>n</i> -BuH, 49.60	5	11	42.40	101.3	+1.5
84.0	B-2, 49.45; <i>n</i> -BuH, 49.25	1	12 <sup>c</sup>	49.70	100.5	+0.7
84.0	B-2, 49.90; <i>n</i> -BuH, 50.10	10	17	29.30	100.3	+0.5
84.0	B-2, 49.90; <i>n</i> -BuH, 49.00	9	13	29.00	100.2	+0.4
82.0	B-2, 50.50; <i>n</i> -BuH, 49.45	7	28	41.45	100.3	+0.5
82.0	B-2, 50.80; <i>n</i> -BuH, 49.20	8	27	18.30	100.2	+0.4
79.9	B-2, 49.50; <i>n</i> -BuH, 50.25	11	47	14.60	100.0	+0.2
77.5	i-B, 50.20; N <sub>2</sub> , 49.90	5	10	44.80	99.6	...
77.5	i-B, 49.45; N <sub>2</sub> , 51.10	3	10	49.10	99.6	...
77.5	i-B, 51.10; <i>n</i> -BuH, 49.30	1	10 <sup>d</sup>	53.35	104.4	+4.8
77.5	i-B, 49.90; <i>n</i> -BuH, 49.85	6	10	46.90	101.1	+1.5

<sup>a</sup> B-1 = 99.6% butene-1; B-2 = 99.8% butene-2; i-B = 99.6% isobutylene.  
<sup>b</sup> Absorption was incomplete; additional passes removed about 0.2 cc. per pass.  
<sup>c</sup> Additional passes removed about 0.05 cc. per pass.  
<sup>d</sup> Additional passes removed about 0.3 cc. per pass.

about 90 per cent is negligibly small. In stronger acids it can be fairly large. Obviously, the use of small portions of acid (7) is superior to that of the large volumes sometimes employed.

PHYSICAL SOLUTION IN ABSORPTION PRODUCTS. In the analyses of synthetic mixtures given in Table II, the errors noted were due to the increase produced in the solvent power of the acid for *n*-butane by dissolved olefin-absorption products. Acid portions of 1.0 cc. were used; but as approximately 1 cc. could not be removed and replaced because of wetting of the walls of the pipet and the contact tubes, a total of 2 cc. was present. The effect of solubility in the absorbent itself was eliminated by previous saturation of the first portion with *n*-butane and by use of the solubility data already presented for estimation of corrections for subsequent portions. The magnitude of the error decreased with de-



TABLE IV. INFLUENCE OF OVERSTRONG ACID ON OLEFIN DETERMINATIONS

H <sub>2</sub> SO <sub>4</sub> %	Gases <sup>a</sup> Taken Cc.	1-Cc. Acid Por- tions	30- Sec. Passes	Max. Ab- sorbed per Portion	Olefin %	Error %	H <sub>2</sub> SO <sub>4</sub> %	Gases <sup>a</sup> Taken Cc.	1-Cc. Acid Por- tions	30- Sec. Passes	Max. Ab- sorbed per Portion	Olefin %	Error %
104.0 <sup>b</sup>	E, 79.60; N <sub>2</sub> , 20.20	1	6 <sup>c</sup>	75.10	94.4	-5.4	91.4	B-1, 49.65; N <sub>2</sub> , 50.00	2	2	48.20	98.9	-0.7
104.0	E, 50.70; N <sub>2</sub> , 49.65	1	4 <sup>c</sup>	47.55	93.7	-6.1	91.4	B-1, 50.20; N <sub>2</sub> , 49.35	3	3 <sup>e</sup>	44.15	98.8	-1.0
104.0	E, 50.55; N <sub>2</sub> , 49.60	5	5	28.90	97.0	-2.8	90.3	B-1, 49.80; N <sub>2</sub> , 50.20	1	3 <sup>c</sup>	49.25	98.6	-0.8
102.0 <sup>d</sup>	E, 79.80; <i>n</i> -BuH, 19.80	1	10 <sup>c</sup>	77.95	97.7	-2.1	90.3	B-1, 49.00; N <sub>2</sub> , 49.60	3	3	46.80	98.8	-0.8
102.0	E, 50.60; N <sub>2</sub> , 49.10	1	10	49.45	97.7	-2.1	90.3	B-1, 49.80; N <sub>2</sub> , 49.15	4	4 <sup>e</sup>	39.40	99.1	-0.5
102.0	E, 79.70; N <sub>2</sub> , 19.70	1	8 <sup>c</sup>	77.90	97.8	-2.0	96.3	B-2, 49.30; N <sub>2</sub> , 50.65	1	2 <sup>c</sup>	48.65	98.4	-1.4
102.0	E, 50.20; N <sub>2</sub> , 49.80	5	9	23.00	97.8	-2.0	96.3	B-2, 50.30; N <sub>2</sub> , 50.05	1	4 <sup>c</sup>	...	97.5	-2.3
102.0	E, 49.45; <i>n</i> -BuH, 49.30	5	7	30.30	98.5	-1.3	96.3	B-2, 49.65; N <sub>2</sub> , 49.70	2	2	49.00	98.8	-1.0
102.0	E, 49.60; N <sub>2</sub> , 50.25	6	8 <sup>e</sup>	13.70	99.8	0.0	96.3	B-2, 49.75; N <sub>2</sub> , 50.60	2	2 <sup>e</sup>	46.90	99.2	-0.6
99.7	E, 49.60; N <sub>2</sub> , 50.10	1	20	49.50	99.8	0.0	94.0	B-2, 49.75; N <sub>2</sub> , 50.60	1	2 <sup>c</sup>	49.40	98.9	-0.9
99.7	E, 57.00; N <sub>2</sub> , 50.20	1	28	106.45 <sup>f</sup>	99.8	0.0	94.0	B-2, 49.65; N <sub>2</sub> , 49.70	1	4 <sup>c</sup>	...	97.9	-1.9
99.7	E, 49.90; N <sub>2</sub> , 50.00	4	19	17.55	99.8	0.0	94.0	B-2, 49.70; N <sub>2</sub> , 50.30	2	2	48.40	99.0	-0.8
96.3	P, 49.75; N <sub>2</sub> , 49.55	1	2 <sup>c</sup>	48.30	97.1	-0.3	94.0	B-2, 49.70; N <sub>2</sub> , 50.30	2	2 <sup>e</sup>	47.20	99.4	-0.4
96.3	P, 51.45; N <sub>2</sub> , 49.90	1	4 <sup>c</sup>	...	96.9	-0.5	91.4	B-2, 50.45; N <sub>2</sub> , 49.80	1	2 <sup>c</sup>	50.30	99.4	-0.4
96.3	P, 49.45; N <sub>2</sub> , 50.15	2	2	50.05	97.3	-0.1	91.4	B-2, 50.20; N <sub>2</sub> , 49.45	1	4 <sup>c</sup>	...	98.7	-1.1
96.3	P, 49.75; N <sub>2</sub> , 49.80	3	3 <sup>e</sup>	42.80	97.4	0.0	91.4	B-2, 49.80; N <sub>2</sub> , 49.15	2	2	49.00	99.3	-0.5
94.0	P, 49.75; N <sub>2</sub> , 49.80	1	3 <sup>c</sup>	48.45	97.4	0.0	90.3	B-2, 50.15; N <sub>2</sub> , 49.75	3	3 <sup>e</sup>	46.90	99.5	-0.3
94.0	P, 49.60; N <sub>2</sub> , 50.95	3	3	47.75	97.4	0.0	90.3	B-2, 50.20; N <sub>2</sub> , 49.50	1	3 <sup>c</sup>	50.05	99.5	-0.3
94.0	P, 49.35; N <sub>2</sub> , 49.60	3	3 <sup>e</sup>	42.55	97.4	0.0	90.3	B-2, 49.55; N <sub>2</sub> , 49.35	3	3	48.80	99.6	-0.2
96.3	B-1, 49.50; N <sub>2</sub> , 50.20	1	2 <sup>c</sup>	48.00	97.0	-2.6	90.3	B-2, 49.55; N <sub>2</sub> , 49.35	4	4 <sup>e</sup>	45.70	99.7	-0.1
96.3	B-1, 50.40; N <sub>2</sub> , 49.60	1	4 <sup>c</sup>	...	95.9	-3.7	96.3	i-B, 49.80; N <sub>2</sub> , 50.75	1	1 <sup>c</sup>	48.65	97.5	-2.1
96.3	B-1, 50.45; N <sub>2</sub> , 49.70	2	2	48.55	97.4	-2.2	96.3	i-B, 50.00; N <sub>2</sub> , 49.30	1	3 <sup>c</sup>	...	96.7	-2.9
94.0	B-1, 50.75; N <sub>2</sub> , 49.30	3	3 <sup>e</sup>	46.95	97.1	-2.5	91.4	i-B, 49.90; N <sub>2</sub> , 50.80	1	6 <sup>c</sup>	...	94.5	-5.1
94.0	B-1, 49.70; N <sub>2</sub> , 50.40	1	2 <sup>c</sup>	49.60	97.6	-2.0	96.3	i-B, 50.15; N <sub>2</sub> , 50.30	2	2	48.20	97.2	-2.4
94.0	B-1, 50.85; N <sub>2</sub> , 49.75	1	4 <sup>c</sup>	...	96.7	-2.9	91.4	i-B, 51.20; N <sub>2</sub> , 49.80	1	2 <sup>c</sup>	49.25	98.5	-1.1
91.4	B-1, 49.35; N <sub>2</sub> , 50.65	2	2	47.75	97.8	-1.8	91.4	i-B, 49.55; N <sub>2</sub> , 49.90	1	4 <sup>c</sup>	...	97.8	-1.8
		3	3 <sup>e</sup>	47.30	98.7	-0.9	90.3	i-B, 49.55; N <sub>2</sub> , 49.90	2	2	48.85	99.0	-0.6
		1	2 <sup>c</sup>	48.55	98.2	-1.4	90.3	i-B, 49.55; N <sub>2</sub> , 49.90	3	3 <sup>e</sup>	48.70	99.1	-0.5
		1	4 <sup>c</sup>	...	97.6	-2.0	90.3	i-B, 49.55; N <sub>2</sub> , 49.90	1	2 <sup>c</sup>	49.20	99.0	-0.6
							90.3	i-B, 49.55; N <sub>2</sub> , 49.90	3	3 <sup>e</sup>	48.00	99.2	-0.4

<sup>a</sup> E = 99.8% ethylene; P = 97.4% propylene; B-1 = 99.6% butene-1; B-2 = 99.8% butene-2; i-B = 99.6% isobutylene.

<sup>b</sup> 104.0% H<sub>2</sub>SO<sub>4</sub> = 100.0% H<sub>2</sub>SO<sub>4</sub> containing 4.0% free SO<sub>3</sub> by weight.

<sup>c</sup> Additional passes increased the residual volume.

<sup>d</sup> 102.0% H<sub>2</sub>SO<sub>4</sub> = 100.0% H<sub>2</sub>SO<sub>4</sub> containing 2.0% free SO<sub>3</sub> by weight.

<sup>e</sup> Special short passes, about 5 seconds long, exclusive of inflow and outflow, were used.

<sup>f</sup> Same portion of acid was used as in preceding analysis.

crease in concentration of acid and with increase in frequency of replacement of acid.

As illustrated by the similarly obtained analyses given in Table III, a similar but much larger error was caused by precipitated polymer products. These, present as a cloudiness or as definite droplets, absorbed *n*-butane with avidity. Although the absorption was one of physical solution, it did not reach completion during the analysis period because of continued precipitation of polymer. The effect was largest when only one portion of absorbent was used throughout the analysis. For such analyses Table III gives the result after twelve 30-second passes; four additional passes increased the apparent percentage of olefin from 102.5 to 104.3 for butene-1 and from 103.4 and 100.5 to 108.9 and 101.3 for butene-2, respectively. No attempt was made to correct the data for the increase in solvent power of the acid caused by dissolved products.

The data of Tables II and III indicate that, if the acid is not too strong and if it is replaced so frequently that absorption is limited to less than about 15 cc. per portion, such physical solubility errors become practically negligible.

UNABSORBABLE GAS LIBERATED BY OVERSTRONG ABSORBENTS. The analyses in Table IV, for which 30-second passes were used except as otherwise stated, illustrate the large errors produced by liberation of gas or vapor unabsorbable in fresh acid or alkali when overstrong acids were used.

The data indicate that, in the analysis of ethylene, if absorption is limited to not more than 15 to 20 cc. per portion, acid up to at least 100 per cent in strength can be used safely. Similarly, the upper limit of safe acid concentration is about 95 per cent for propylene and about 90 per cent for butylenes. Discoloration of the absorbent, except when butadiene is present, indicates, because of liberation of gas, a low analytical result.

The analyses in Table V show that formation of unabsorbable gas is promoted by the presence of silver sulfate.

The data indicate that in the analysis of ethylene, with sufficiently frequent replacement of absorbent, silver sulfate

TABLE V. INFLUENCE OF SILVER SULFATE ON ETHYLENE DETERMINATIONS

H <sub>2</sub> SO <sub>4</sub> %	Ag <sub>2</sub> SO <sub>4</sub> %	Gases <sup>a</sup> Taken Cc.	1-Cc. Acid Por- tions	30- Sec. Passes	Max. Ab- sorbed per Portion	Olefin %	Error %
99.7	0.00	E, 49.60; N <sub>2</sub> , 50.10	1	20	49.50	99.8	...
99.7	0.00	E, 57.00; N <sub>2</sub> , 50.20	1	28	106.45 <sup>b</sup>	99.8	...
99.7	0.50	E, 79.95; N <sub>2</sub> , 19.85	1	12 <sup>c</sup>	78.30	97.9	-1.9
99.7	0.50	E, 80.15; N <sub>2</sub> , 19.70	3	12	54.30	99.4	-0.4
99.7	0.50	E, 79.30; N <sub>2</sub> , 20.30	4	15	38.65	99.6	-0.2
99.7	0.50	E, 79.40; N <sub>2</sub> , 20.60	6	14	28.55	99.6	-0.2
99.7	0.50	E, 81.20; <i>n</i> -BuH, 18.30	9	18	27.70	99.7	-0.1
96.0	1.50	E, 79.55; N <sub>2</sub> , 19.70	1	16 <sup>c</sup>	77.10	96.9	-2.9
96.0	1.50	E, 68.80; N <sub>2</sub> , 32.45	1	8 <sup>c</sup>	66.75	97.0	-2.8
96.0	1.50	E, 49.60; <i>n</i> -BuH, 49.90	6	9	19.95	98.1	-1.7
96.0	1.50	E, 70.85; N <sub>2</sub> , 29.20	6	10	24.10	97.5	-2.3
96.0	1.50	E, 68.35; N <sub>2</sub> , 31.15	7	12	24.80	98.1	-1.7
96.0	1.50	E, 66.25; N <sub>2</sub> , 35.35	11	11 <sup>d</sup>	11.30	99.6	-0.2
96.0	1.00	E, 79.40; N <sub>2</sub> , 20.15	1	36	77.05	97.0	-2.8
96.0	1.00	E, 48.80; <i>n</i> -BuH, 47.80	8	15	13.15	98.9	-0.9
96.0	1.00	E, 81.00; <i>n</i> -BuH, 19.70	10	17	24.60	98.1	-1.7
91.0	1.50	E, 69.75; N <sub>2</sub> , 30.20	16	42	8.90	99.7	-0.1
90.0	1.50	E, 80.15; N <sub>2</sub> , 19.60	15	36	9.40	99.3	-0.5
90.0	1.00	E, 80.45; N <sub>2</sub> , 20.20	22	44	9.45	99.6	-0.2

<sup>a</sup> E = 99.8% ethylene.

<sup>b</sup> Same portion of acid was used as in preceding analysis.

<sup>c</sup> Additional passes increased the residual volume.

<sup>d</sup> Special short passes were used.

in concentrations varying from 0.50 per cent in 100 per cent sulfuric acid to 1.0 per cent in 90 per cent acid can be used. No experiments were made with other catalysts beyond the observation that neither mercury sulfate nor nickel sulfate appeared to accelerate the absorption of ethylene by 96 per cent sulfuric acid.

### Basic Scheme of Improvement

In the past, the sulfuric acid method has been capable of giving accurate results only for relatively small concentrations of olefins. Large concentrations, because of the limitations described, have led to positive and negative errors of unpredictable magnitude. The chief improvement to be made is the automatic minimization of these errors to the point at which they are negligible.



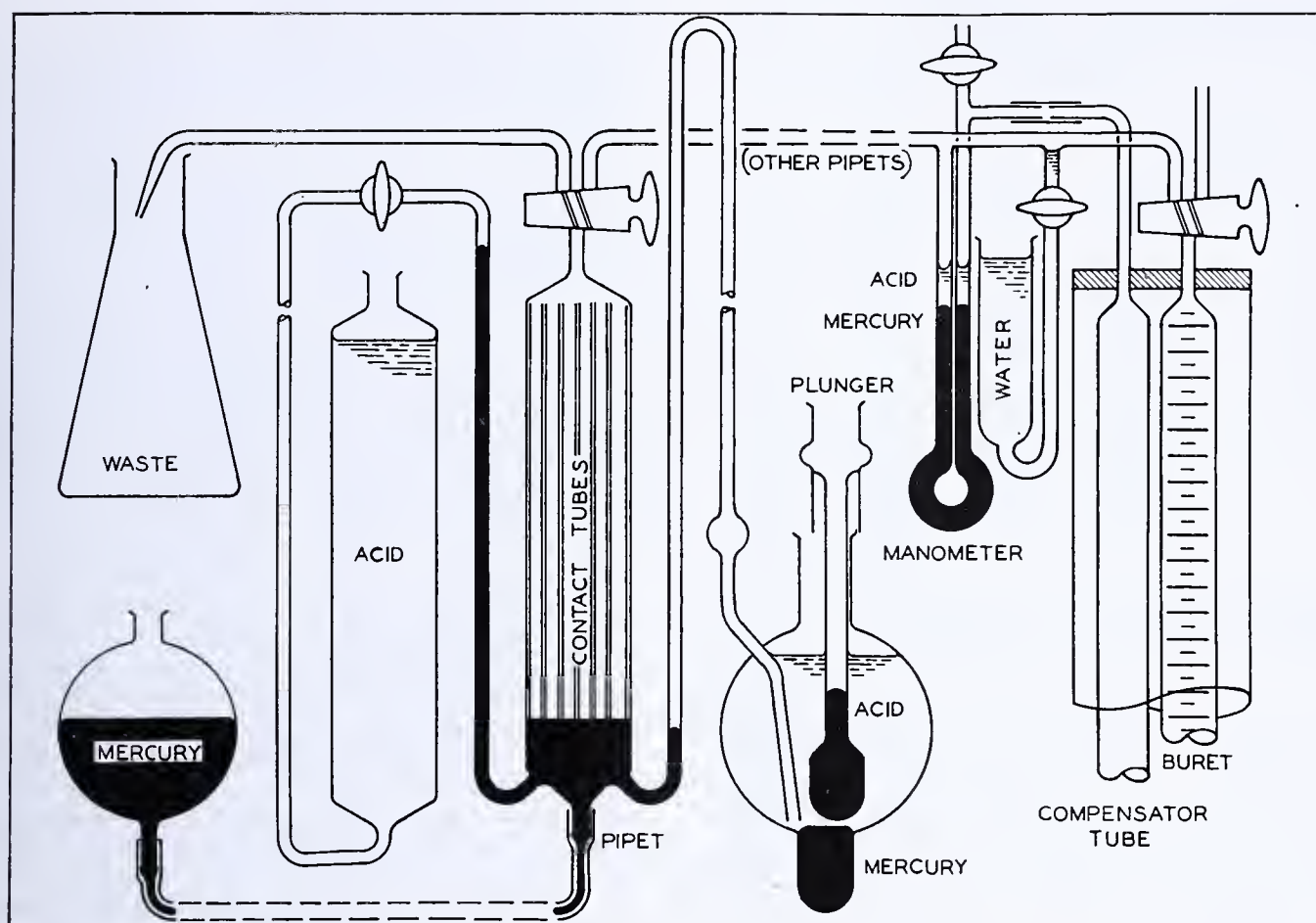


FIGURE 2. APPARATUS FOR SULFURIC ACID ANALYSIS OF GASEOUS OLEFINS

Although in many cases the obvious expedient of dilution of the sample with an inert gas is applicable, a generally more satisfactory scheme, in combination with the technic of frequent replacement of absorbent, is the use of a preliminary absorbent so weak that it requires no correction for incomplete specificity, to reduce the concentration of the olefin to the point at which a stronger final absorbent can be used reliably.

### Absorbents

For determination of gaseous olefins to within 0.2 per cent, the absorbents specified in Table VI are satisfactory.

TABLE VI. ABSORBENTS RECOMMENDED FOR DETERMINATION OF GASEOUS OLEFINS

Olefin	Preliminary Absorbent	Final Absorbent
Isobutylene	60-62% H <sub>2</sub> SO <sub>4</sub>	68-70% H <sub>2</sub> SO <sub>4</sub>
n-Butenes, propylene	80-82% H <sub>2</sub> SO <sub>4</sub>	88-90% H <sub>2</sub> SO <sub>4</sub>
Ethylene	88-90% H <sub>2</sub> SO <sub>4</sub> + 0.9-1.0% Ag <sub>2</sub> SO <sub>4</sub>	98-100% H <sub>2</sub> SO <sub>4</sub> + 0.4-0.5% Ag <sub>2</sub> SO <sub>4</sub>

The higher figure given in each range is considered to be the maximum permissible value. Intermediate and lower concentrations can be used. For example, concentrated sulfuric acid containing up to 0.7 per cent silver sulfate can be used as a final absorbent for ethylene.

The solutions are prepared in accordance with the equality  $A = WS/(C - S)$ , in which  $A$  is the weight of concentrated acid containing  $C$  per cent sulfuric acid to be added to the weight,  $W$ , of ice to yield a solution of  $S$  per cent sulfuric acid. For acid of specific gravity 1.84,  $C$  varies from about 94 to over 96; its exact value can be calculated from the strength, found by specific gravity measurement, of a solution prepared from known weights of acid and ice. The 98 to 100 per cent acid is prepared by the addition of fuming acid to concentrated acid. A portion should be tested with a 100-cc. sample of air; if it increases the volume of air in two passes by more than 0.05 cc., it should be diluted with a little concentrated acid.

### Apparatus

The apparatus shown in Figure 2, designed for rapid replacement of small portions of absorbent, is highly satisfactory. A contact-type absorption pipet is connected at its top through a three-way stopcock to the manifold of a gas-analysis assembly and at its bottom through a rubber tube to a leveling bulb containing mercury. Small siphons lead from its bottom to sulfuric acid reservoirs, of which two types suitable for acids of up to 100 per cent in strength are shown. When the siphon stopcock for one is open or when the plunger for the other is in the elevated position shown, acid is drawn into the pipet by lowering of the leveling bulb.

Because mercury slowly displaces silver from silver sulfate, sulfuric acid containing this catalyst is kept in glass-stoppered bottles from which portions are drawn directly into the pipet through the discharge arm of the pipet stopcock. If all absorbents are handled in this way, acid reservoirs need not be incorporated in the gas-analysis assembly. No lubricant other than the acid itself is used for the stopcocks.

As is indicated by Figure 2, the manometer stopcock customary to Orsat-type assemblies can be omitted.

### Choice of Analytical Conditions

**SIZE OF ACID PORTIONS.** The amount of absorbent taken at a time should be about 1 cc. As is illustrated by the two sets of analytical details in Table VII, one obtained with replacement of acid (1.0 cc.) above the mercury after every two passes of 30 seconds each and the other with one portion of 5 to 6 cc. of each acid, exclusive of acid clinging to the contact tubes, larger portions do not increase the absorption rate appreciably.

In order that the absorbent may spread over the contact tubes sufficiently rapidly, each successive small portion should not be less than 1 cc. As the absorbent clinging to the walls of the pipet and the contact tubes approximates 1 cc., the total volume in the pipet is about 2 cc. The top of the pipet should be marked at the 1.0-cc. point; but no great striving to obtain portions of exactly this size is necessary.

Incidentally, the first analysis in Table VII illustrates the uncertainty involved when a single acid of the strength usually recommended is used for the determination of an olefin at as



TABLE VII. INDEPENDENCE OF ABSORPTION RATE AND ACID VOLUME

H <sub>2</sub> SO <sub>4</sub> %	No. of Passes	Many 1.0-Cc. Portions <sup>a</sup> Reading Absorbed Cc.	One 5- to 6-Cc. Portion <sup>b</sup> Reading Absorbed Cc.
64.3	0	100.35	99.50
	2	85.60	84.70
	2	74.25	74.00
	2	67.15	67.15
	2	63.30	63.00
	2	61.40	60.80
	2	60.50	59.70
	2	60.00	59.20
	2	59.70	58.80
	2	59.40	58.50
	2	59.20	58.20
	2	58.95	57.90
	2	27.00	24.80
	2	21.90	21.35
84.3	2	20.65	20.50
	2	20.30	20.20
	2	20.20	20.10
	2	20.20	20.00
	2	20.20	19.95
	2	...	19.90
	2	...	19.80
	2	...	...
	2	...	...
	2	...	...

Composition of sample, cc.:

<sup>a</sup> Isobutylene 39.40, butene-2 40.70, *n*-butane 20.25.<sup>b</sup> Isobutylene 38.70, butene-2 40.45, *n*-butane 20.35.

high a concentration as 40 per cent: the isobutylene found was  $(100.35 - 58.95) - 11 \times 0.25 = 38.65$  cc., whereas 39.40 cc. were taken; the butene-2 found was  $(58.95 - 20.20) + 11 \times 0.25 = 41.50$  cc., whereas 40.70 cc. were taken.

In the second analysis the isobutylene found was  $(99.50 - 57.90) - 11 \times 0.30 = 38.30$  cc., whereas 38.70 cc. were taken. This result, because of a fortuitous compensation of errors, is better than that in the first analysis; it should not be interpreted as indicating that the use of a large portion is superior to the use of several small portions. The inferiority of the use of the single portion is shown by the butene-2 determination, in which the absorption did not reach the sharp end point obtained when fresh acid was always present. The small final absorption rate, like those mentioned in the footnotes of Table III, was due to physical solution of butane by the polymers that were being formed. After polymer formation had continued overnight, the residual volume of 19.80 cc. decreased in two passes to a constant value of 14.00 cc.; thus, the polymers from 40.45 cc. of butene-2 physically dissolved 6.35 cc. of *n*-butane. As ethylene was known to be absent, the absorption might have been continued to this ultimate end point, which would have indicated a butene-2 content of  $(57.90 - 14.00) + 11 \times 0.30 = 47.20$  cc., whereas 40.45 cc. were taken. If ethylene had been present, differentiation of the absorption of ethylene from the solution of butane by the polymers would have been impossible—a dilemma avoided by the use of multiple portions.

**DURATION OF PASSES.** The passes of the gas sample into the absorption pipet must be made in a standard manner, with all passes alike. Very short passes, because of the large number required, produce a troublesome desiccation of the upper part of the buret. Very long passes, because of drainage from the contact tubes, produce a decreased over-all rate of absorption. This effect is illustrated by the absorption data in Table VIII for 50 per cent isobutylene and 69.5 per cent sulfuric acid. Replacement of acid was made after each buret reading.

Inclusive of the average of 5 seconds spent in each passage of gas between buret and pipet, the first absorption required  $14 \times (30 + 10) = 560$  seconds; the second required  $8 \times (75 + 10) = 680$  seconds. Complete absorption required 23 per cent more time for the 75-second passes than for the 30-second passes.

A pass during which the sample is kept in the absorption pipet for 30 seconds is highly satisfactory.

**REPLACEMENT SCHEDULE.** For the absorbents specified in Table VI and for 30-second passes, replacement of absorbent after every two passes is satisfactory.

**PIPET WASHING.** Since correction for incomplete specificity of a final absorbent can be made accurately only if the absorbent strength is constant, two or three 1- to 2-cc. portions of such absorbent must be used prior to absorption to

wash any weaker acid from the pipet. To spread the acid over the contact tubes, air is drawn in through the acid-discharge tube. When, however, a preliminary absorbent is to be used, pipet-washing is preferably omitted. This has the advantage, important for samples of high olefin content, especially of *n*-butenes, that the absorption by the first few portions, which undergo dilution, is kept from exceeding about 15 cc. per portion.

After each analysis, the pipet is washed once with about 5 cc. of water, which is first run into the adjacent part of the manifold to remove any acid accidentally carried there.

**MOISTURE.** Several considerations indicate that buret readings should be made with the sample saturated with moisture: (1) No preliminary desiccation of moisture-containing samples is then necessary; (2) it is next to impossible to keep an Orsat apparatus reliably dry, because of the aqueous solutions and the moisture from combustions; (3) sulfuric acid solutions have an appreciable aqueous tension, which varies with concentration and temperature and for which correction (6, 10) requires time-consuming calculations; and (4) the simplest method of taking account of the aqueous tension of absorbents or of moisture in the sample is the automatic saturation of the sample with water vapor in the buret.

Because sulfuric acid has a strong desiccating action, careful attention must be paid to keeping sufficient water in the buret. If the rapid or short passes customary to Orsat analyses are used, desiccation of the upper part of the buret and the resultant unsaturation can produce a not inconsiderable error. Even when sufficient water is present in the buret, such an error can occur unless the sample is kept in the absorption pipet long enough for a part of the water to work its way up to the top of the buret.

For addition of water to the buret during the course of an analysis, a small water-reservoir connected through a stopcock to the manifold between the buret and the manometer, as in Figure 2, is convenient.

TABLE VIII. INFLUENCE OF DRAINAGE ON TIME OF ABSORPTION OF ISOBUTYLENE

30-Second Passes			75-Second Passes		
No. of passes	Buret reading	Absorbed Cc.	No. of passes	Buret reading	Absorbed Cc.
0	99.90	...	0	100.00	...
2	63.10	36.80	1	69.95	30.05
2	52.00	11.10	1	55.10	14.85
2	50.30	1.70	1	51.10	4.00
2	50.10	0.20	1	50.25	0.85
2	50.05	0.05	1	50.10	0.15
2	50.00	0.05	1	50.05	0.05
2	50.00	0.00	1	50.00	0.05
			1	50.00	0.00

**DILUTION.** Since the residual volume after analysis should not be less than 15 to 20 cc., the sample must be diluted with air or nitrogen if it contains more than 85 per cent of olefins. About 15 to 20 cc. of diluent are taken, measured, and stored in the sulfuric acid pipet. Then 80 to 85 cc. of the sample are taken; this is preferably but not necessarily measured, and is diluted by adding the diluent to it. After mixing is effected by raising the leveling bulb for the buret a few times, the buret being closed at the top if the manometer is open to the manifold, the total volume is measured. In order to minimize the effect of deviations from the gas laws, the volume of the sample should be taken as the difference between the volumes of the mixture and the diluent instead of that directly measured before dilution.

### Absorption Procedure

After a 1-cc. portion of the appropriate preliminary absorbent is placed above the mercury in the pipet, two 30-second passes of the accurately measured gas sample are made. Then the acid is drawn up to the pipet stopcock, which is turned to discharge the



spent acid, and the gas volume is read. This procedure is repeated until the absorption per portion of full-strength preliminary absorbent becomes less than 5 cc. In this manner, the residual olefin is reduced to 5 to 15 cc. (sometimes more than 15 cc. if the olefin is ethylene). If the pipet previously contained a weaker acid, at least two or three portions should be used before the preliminary absorption is discontinued. If the sample is known to contain less than about 15 cc. of the olefin, the preliminary absorbent should not be used at all.

Then the pipet is washed at least twice with the corresponding final absorbent and absorption is continued with two 30-second passes into each portion of fresh absorbent until a constant small absorption is obtained for about three portions (only one or two portions if it is zero). A total of 5 to 8 portions is generally required.

After the constant absorption has been determined, the foregoing procedure is repeated for the next set of absorbents.

The buret readings need not be made with accuracy until the rate of absorption is small. This condition is indicated independently by a transition, pronounced for the olefins heavier than ethylene, from a "rough" appearance of the acid on the contact tubes to a "smooth" appearance.

### Corrections

In general, physical solubility of gaseous paraffins is more than negligible only in the final absorption of ethylene. A correction for it is found by continuation of the absorption until it becomes constant for each 1-cc. portion of final absorbent and multiplication of the constant absorption by the number of portions.

TABLE IX. ABSORPTION OF UNDILUTED OLEFINS IN TWO 30-SECOND PASSES

H <sub>2</sub> SO <sub>4</sub> , %	Butene-2 (99.8%)	Butene-1 (99.6%)	Propylene (97.4%)	Ethylene (99.8%)
62.0	0.20	0.15	..	0.025
70.0	2.15	1.25	1.15	0.05
82.0	..	..	..	0.90
90.0	..	..	..	..

In the analysis of samples containing principally four-carbon hydrocarbons, an appreciable physical solubility effect can be present also during the use of 88 to 90 per cent acid. If both butanes are present in considerable amounts, or if the temperature happens to be much below 25° C., it can amount to even more than that indicated by Table I—e. g., 0.05 cc. per 1-cc. portion of acid. In such analyses, especially when ethylene is known to be absent, corrections should be determined in the manner just described.

The same procedure is used to obtain corrections for incomplete specificity of absorbents for olefins heavier than ethylene. As indicated by Table IX, which gives the absorption obtained in two 30-second passes of about 100 cc. of substantially pure olefin into acids of the maximum recommended strengths, the correction is largest for butene-2 absorbed at the end of the isobutylene determination.

In actual analyses, because of dilution of olefins with other gases and generally smaller effective acid-surface areas, the absorptions indicated in Table IX are never obtained.

As alkali solutions dissolve paraffins to a considerable extent and as the absorbents here recommended are nonfuming, the usual procedure of passing the gas residue from the ethylene absorption into an alkali pipet, which is necessary in determinations by fuming acid, should not be used.

### Examples

A typical example illustrating the use and the accuracy of the improved method is presented in Table X. The pipet was washed out twice with 1 to 2 cc. of acid of each new concentration before the acid was used for absorption. Buret readings and replacement of absorbent were made after every two passes of 30 seconds each (exclusive of time of inflow and outflow).

The accuracy is all that can be expected. In a series of analyses of synthetic mixtures of four-carbon hydrocarbons,

TABLE X. ANALYSIS OF SYNTHETIC MIXTURE OF GASEOUS OLEFINS

Time	H <sub>2</sub> SO <sub>4</sub> %	Reading Cc.	Absorbed Cc.	Time	H <sub>2</sub> SO <sub>4</sub> %	Reading Cc.	Absorbed Cc.
2:14	..	100.00	..	3:13	90.0	44.80	9.05
	62.0	93.20	6.80		90.0	44.50	0.30
	62.0	86.40	6.80		90.0	44.25	0.25
	62.0	81.60	4.80		90.0	44.00	0.25
2:28	70.0	75.50	6.10		90.0	43.75	0.25
	70.0	74.05	1.45	3:30	90.0 Ag <sup>a</sup>	38.15	5.60
	70.0	73.40	0.65		90.0 Ag	34.00	4.15
	70.0	72.80	0.60	3:40	100 Ag <sup>b</sup>	25.60	8.40
	70.0	72.30	0.50		100 Ag	21.10	4.50
	70.0	71.80	0.50		100 Ag	19.75	1.35
	70.0	71.40	0.40		100 Ag	19.45	0.30
	70.0	70.90	0.50		100 Ag	19.25	0.20
2:59	82.0	62.70	8.20		100 Ag	19.10	0.15
	82.0	57.65	5.05		100 Ag	18.90	0.20
	82.0	53.85	3.80	4:01	100 Ag	18.70	0.20

<sup>a</sup> 90.0 Ag = 90.0% H<sub>2</sub>SO<sub>4</sub> containing 1.00% Ag<sub>2</sub>SO<sub>4</sub>.

<sup>b</sup> 100 Ag = 100% H<sub>2</sub>SO<sub>4</sub> containing 0.50% Ag<sub>2</sub>SO<sub>4</sub>.

Calculations:

Isobutylene found = 100.00 - (70.90 + 8 × 1.90/4)	= 25.30%
Isobutylene taken	= 25.30%
Difference	= 0.00%
<i>n</i> -Butenes + propylene found = (70.90 + 8 × 1.90/4) - (43.75 + 5 × 0.25)	= 29.70%
Butene-2 + propylene taken = 14.75 + 14.75	= 29.50%
Difference	+0.20%
Ethylene found = (43.75 + 5 × 0.25) - (18.70 + 8 × 0.75/4)	= 24.80%
Ethylene taken	= 24.90%
Difference	= -0.10%
Paraffins and inerts found = 18.70 + 8 × 0.75/4	= 20.20%
<i>n</i> -Butane and inerts taken = 19.60 + 0.60	= 20.20%
Difference	= 0.00%

the value for *n*-butenes appeared to be consistently slightly too high, probably because of the individually negligible but cumulatively appreciable solution of butane in the 15 to 20 portions of acid that were used. Hence, when the residual gas is known to consist mainly of one or both butanes, it appears justifiable to subtract a small supplementary and somewhat arbitrary correction of 0.10 cc. from the value for the *n*-butene fraction. In the present example, this reduces the difference between the amounts found and taken from 0.20 to 0.10 per cent.

TABLE XI. ANALYSIS OF SYNTHETIC BUTENE-2

Air taken	= 17.70 cc.
Butene-2 taken	= 81.80 cc.
Total, calculated	= 99.50 cc.
Total, measured	= 99.60 cc.
Sample volume = 99.60 - 17.70	= 81.90 cc.

Time	H <sub>2</sub> SO <sub>4</sub> %	Reading Cc.	Absorbed Cc.	Time	H <sub>2</sub> SO <sub>4</sub> %	Reading Cc.	Absorbed Cc.
9:00	..	99.60	..		82.0	63.50	15.70
	70.0	97.55	2.05		82.0	48.10	15.40
	70.0	96.05	1.50		82.0	36.90	11.20
	70.0	94.60	1.45		82.0	29.70	7.20
	70.0	93.20	1.40		82.0	25.10	4.60
	70.0	91.80	1.40	9:37	90.0	18.00	7.10
	70.0	90.40	1.40		90.0	17.90	0.10
9:20	82.0	79.20	11.20	9:43	90.0	17.90	0.00

Calculations:

Isobutylene found = 99.60 - (90.40 + 6 × 1.40)	= 0.80 cc. = 1.0%
Butene-2 found = (90.40 + 6 × 1.40) - 17.90	= 80.90 cc. = 98.8%
Inert impurities found = 17.90 - 17.70	= 0.20 cc. = 0.2%

Table XI illustrates the analysis of one of the most difficult samples likely to be encountered, butene-2 (prepared from the corresponding technical alcohol) containing a small concentration of isobutylene. The pipet was first washed 3 or 4 times with the 70.0 per cent acid. No pipet-washing was made with the 82.0 per cent acid; hence, no portion absorbed much in excess of 15 cc. of butene-2. As ethylene was known to be absent, no pipet-washing was made with the 90.0 per cent acid.

In spite of the high final constant absorption rate of 1.40 cc. per portion, no appreciable uncertainty was present in the



isobutylene determination. In the absence of isobutylene, the rate would have been constant from the very first. Whenever this synthetic butene-2 was used, its known content of isobutylene was taken into account or, if necessary, as for the determination of the data in Table IX, the isobutylene was first removed with 68 to 70 per cent acid. The other olefin samples contained no extraneous olefin; the impurities were the corresponding paraffins or air.

The time required for an analysis depends somewhat on the details of the apparatus and on the skill of the operator. It is about half an hour for each olefin. For the foregoing two analyses, all absorbents were in bottles, as each had been adjusted to the maximum recommended strength; hence, the total time, because of additional manipulations, was slightly greater than if the reservoirs of Figure 2 had been used.

### Modifications

It is perhaps obvious that some modifications in the method may be made without introducing errors for samples of more or less known composition. For example, in the analysis of samples having small concentrations of olefins, only one concentration of acid need be used for each olefin. Also, the number of passes per portion of acid, especially in determinations of propylene and ethylene, may be increased. Isobutylene in samples containing much butene-2 or much

butadiene can be determined with a somewhat advantageously increased specificity with acids weaker than 68 to 70 per cent. The data presented should prove helpful in selecting conditions for such modifications. For the analysis of any sample in general, however, it is believed that the recommendations given represent an optimum over-all compromise among the several conflicting factors involved and that observance of them will yield rapid and reliable analytical results.

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# Volatilizing Chromium as Chromyl Chloride

## A Rapid Method Applicable to Determination of Manganese in Stainless Steel

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A new and rapid method is described for the accurate determination of manganese in stainless and other high-chromium steels, in which the chromium is rapidly volatilized from a perchloric acid solution of the sample. The method is also applicable to other determinations in which large quantities of chromium are objectionable.

CHROMIUM, when present to the extent of more than 2 or 3 per cent, interferes with the determination of manganese by the persulfate-arsenite method. Consequently, high-chromium steels require a separation of chromium prior to the determination of manganese.

Heretofore, the author has used the zinc oxide separation, which is effected by adding zinc oxide paste to a dilute sulfuric acid solution of the steel which has been oxidized by nitric acid. The mixture containing ferric and chromium hydroxides and the excess zinc oxide is diluted to 200 ml., and filtered, and the manganese is determined on an aliquot of the filtrate. This method is time-consuming for two reasons: Two-gram samples of stainless steels may require from 0.5 to 2 hours to dissolve in 9 *N* sulfuric acid, and the subsequent filtration of the bulky precipitate formed by the zinc oxide is also slow. The author first attempted to overcome this drawback by using perchloric acid to dissolve the steel, which makes solu-

tion possible in 5 to 10 minutes. He also confirmed the experience of other chemists in this laboratory that if oxidation of the iron following solution in sulfuric acid is postponed until after the separation of chromium, the filtration is much faster. An attempt to combine these two improvements by reducing the iron with sulfurous acid after solution in perchloric acid indicated that it is very difficult, from a practical analytical viewpoint, to keep the iron in the reduced state in perchloric acid solution.

The object of the first part of this investigation was to find a means of speeding up the preliminary operations of dissolving the steel and separating the chromium. A possible solution of this problem was suggested by a consideration of the possibility of removing chromium by conversion to a gaseous rather than a solid compound. The formation of the red gas chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , was studied for this purpose. The fact that chromyl chloride can be evolved from a mixture of a solid chloride and potassium dichromate in hot concentrated sulfuric acid is known from the old qualitative test used to distinguish chlorides from bromides. In this test the gases evolved, bromine from bromides and chromyl chloride from chlorides, are absorbed in a dilute ammonium hydroxide solution. The ammonium bromide and hypobromite formed are colorless, while the chromyl chloride forms yellow chromate ions. It follows that the addition of a solid chloride to a hot sulfuric acid solution of hexavalent chromium will volatilize some of the chromium and it is possible that the reaction may be driven nearly to completion by excess of salt, provided that the chromium which is reduced to the trivalent



stage is reoxidized. As shown below, this is done by fuming with perchloric acid between salt additions.

Perchloric acid with a little hydrochloric acid will dissolve stainless steel in 5 to 10 minutes and the chromium is oxidized to the hexavalent state by a few minutes of fuming. The addition of sulfuric acid followed by 0.5 gram of sodium chloride gave a copious evolution of a red gas. An early experiment showed that the sulfuric acid was not necessary for the volatilization of chromyl chloride if the steel is dissolved in perchloric acid. Experimentation was then directed to determine if chromium could be sufficiently volatilized as chromyl chloride with sodium chloride from a perchloric acid solution, so that manganese could be determined accurately.

In further experiments the chromium not volatilized was determined in the perchloric acid solution of stainless steel remaining after the sodium chloride treatment, and a technique was finally developed for volatilization of 99 per cent of the chromium present in the original sample. Where a high concentration of sodium salts is undesirable, a somewhat longer but nearly as effective method of volatilizing the chromium was developed, using hydrochloric acid instead of sodium chloride.

In the third phase of this investigation, the effect of the perchloric acid-sodium chloride treatment decided upon as suitable for application in the determination of manganese was studied for 20 other elements to reveal possible interference of this treatment in the determination of these elements.

Determination of Manganese

Preliminary experiments indicated that the volatilization of chromium could be effected and controlled by adding 2 to 4 grams of solid sodium chloride in 0.5-gram portions after the chromium had been oxidized by the perchloric acid. Following this treatment, the determination of manganese could be completed by the well-known persulfate-arsenite method.

PROCEDURE. To a 1-gram sample in a 500-ml. Erlenmeyer flask add 5 ml. of 6 N hydrochloric acid and 20 ml. of perchloric acid (70 to 72 per cent). Place the flask upon a hot plate to heat rapidly until the steel is dissolved and the chromium is oxidized. Allow the solution to fume 1 minute after oxidation of the chromium to the red hexavalent form. Add 2 to 4 grams of solid sodium chloride in small portions on a spatula or a glass spoon. Make two additions of the salt after the last evolution of the red chromyl chloride. Boil 1 minute after the condensing vapors have washed most of the salt around the neck of the flask down into the solution.

Add cautiously 20 ml. of a mixture of 250 ml. of nitric acid, 125 ml. of 85 per cent phosphoric acid, 185 ml. of 50 per cent sulfuric acid, and 440 ml. of water. Boil 1 minute. Test the solution to make sure it is free of chlorides at this stage by adding a few drops of 1 per cent silver nitrate solution. If necessary, continue the boiling until the solution is chloride-free. Add 10 ml. of 1 per cent silver nitrate solution, 100 ml. of hot water, and 5 ml. of 20 per cent ammonium persulfate solution. When the solution boils, add 10 ml. more of 20 per cent ammonium persulfate solution and boil 30 seconds. Cool rapidly in a water bath and titrate with standard sodium arsenite solution.

The flask need not be removed from the hot plate until the solution is ready for the cooling bath, but the fingers should be kept well away from the neck of the flask when adding the

TABLE I. COMPARISON OF OLD AND NEW METHODS

Sample	Composition of Sample							Manganese Found	
	C %	P %	S %	Si %	Ni %	Cr %	Ti %	ZnO method %	NaCl method %
A	0.07	...	...	...	9.45	17.4	0.496	0.42	0.42, 0.42, 0.42, 0.42
B	0.07	0.020	0.008	0.24	9.00	18.98	...	0.38	0.37, 0.37
C	0.95	0.014	0.008	0.26	0.24	0.15	...	0.31	0.30, 0.31
D-1	0.19	0.013	0.006	0.58	0.73	27.27	...	0.42	0.42, 0.42
D-2	...	...	...	...	...	...	...	...	0.43, 0.43
E-1	0.06°	0.022	0.006	0.25	11.36	18.45	...	0.56	0.54, 0.54
E-2	...	...	...	...	...	...	...	...	0.53, 0.53
F	0.05	0.012	0.008	0.35	9.95	17.63	...	0.59	0.59, 0.59
G	(0.60% Mo, 0.09% Al)		...	...	0.16	5.03	0.49	0.39	0.40, 0.40
H-1	...	...	...	...	9.03	19.14	...	0.40	0.41
H-2	...	...	...	...	...	...	...	0.39	0.40
I	...	...	...	...	8.63	17.45	...	0.38	0.37, 0.38
J	...	...	...	...	9.00	18.65	...	0.45	0.45, 0.47
K	...	...	...	...	9.95	17.63	...	0.59	0.61, 0.61
L	...	...	...	...	9.48	17.28	...	0.38	0.38, 0.39
M	...	...	...	...	8.49	17.93	...	0.35	0.33, 0.36
Bureau of Standards No. 101, certificate value for Mn 0.555								...	0.55, 0.56
Bureau of Standards No. 73, certificate value for Mn 0.276								...	0.26, 0.26

acid mixture to avoid burns by the steam generated from the water in the acid mixture.

Minor variations from the above procedure do not affect results appreciably. The essential precautions are to be sure that the steel is completely dissolved and that the chromium is sufficiently eliminated. Excessive acid concentration interferes with the oxidation of manganese by silver nitrate and ammonium persulfate and, therefore, should be avoided. In the case of steels that are dissolved with difficulty, any further addition of perchloric acid necessary to keep the salts in solution should be held at a minimum, preferably no more than 5 ml. The addition of 10 ml. excess of perchloric acid just before dilution led to low results. Slightly low results, presumably due to peroxide formation, are avoided by the first addition of ammonium persulfate immediately after dilution. For steels containing 0.5 to 2 per cent of silicon, a few drops of hydrofluoric acid aid in their solution.

It is advisable to use 0.5-gram samples for determining manganese when 0.80 to 1.50 per cent of manganese is present in the steel. For these smaller samples the same quantities of acids may be used.

Judging the completeness of the volatilization of chromium by the color of the solution is deceptive for two reasons: The addition of salt deepens the color of the iron to a reddish brown which fades as the hydrochloric acid formed is boiled out, and different types of steel give different final colors. The best criterion is the lack of red fumes within a few seconds after an addition of salt. If too much chromium is left in the solution, on the addition of the ammonium persulfate the formation of a yellow solution is first noticed, with a rather slow development of the permanganate color. This fault is also indicated by the indefinite end point and usually by the lack of agreement of the results on duplicate samples. With practice, the volatilization of the chromium to the degree desired is easily effected.

DETERMINATIONS TO TEST THE METHOD. To test the speed and accuracy of this procedure, determinations were made, comparing the results obtained by the new method with those obtained by the zinc oxide method and with values assigned to authoritative standards. The time required for a single determination will vary from 20 to 30 minutes, depending upon the kind of steel. However, the method is well adapted to group determinations. The author alone has made as many as eighteen manganese determinations on stainless steel samples in one hour, with a reproducibility and accuracy as recorded in Table I.

INTERPRETATION OF RESULTS. This procedure affords a rapid and accurate method for the determination of manganese in high-chromium steels. That it provides a fast and



efficient means of eliminating fairly large amounts of chromium is indicated by its effectiveness in reducing the chromium content of a 1-gram sample of the 27 per cent chromium steel to a point where the residual chromium gave no color interference in the titration of manganese.

### Extent of Elimination of Chromium

**SODIUM CHLORIDE TREATMENT.** Inasmuch as the volatilization of chromium was found effective for manganese determination, it was considered desirable to ascertain just how completely it can be eliminated, in order that this method might be used in other determinations in which chromium interferes.

TABLE II. CHROMIUM ELIMINATION BY SODIUM CHLORIDE

Type of Sample	Method of Treatment with Solid NaCl	Cr in Residue %
18% Cr	3 grams all at once	5
	3 grams in portions	0.15-0.40
	3 grams in portions, rinse, plus 1 gram	0.02, 0.04, 0.06
	3 grams in portions, rinse, plus 1 gram	0.04, 0.00, 0.00, 0.00
25% Cr	5 grams in portions, rinse, plus 3 grams	1.23 (av.)
	5 grams in portions, rinse, plus 3 grams, rinse, plus 2 grams	0.28 (av.)

The amount of chromium remaining after various methods of salting was determined on 1-gram samples of 18 and 25 per cent chromium steels. The results and methods used are indicated in Table II.

After each addition of salt, most of the fumes of chromyl chloride are driven out of the flask and the solid particles are allowed to dissolve before the next addition of salt. The flask or beaker is removed from the hot plate and allowed to cool somewhat before rinsing. The solution is heated to fumes of perchloric acid before subsequent salt additions.

If the sides of the flask or beaker are rinsed after most of the chromium is volatilized, a resalting with 1 gram more of sodium chloride will reduce the amount of chromium from 18 per cent to less than 0.06 per cent. Adding the salt all at once is not effective. Without rinsing, the chromium content is reduced to less than 0.50 per cent, sufficient for manganese determinations. With 25 per cent chromium steels, two rinsings and resaltings are required to lower the chromium to 0.28 per cent. At least 99 per cent of the chromium in the sample can be easily eliminated by using the proper technic, depending upon the amount of chromium present.

TABLE III. ELIMINATION OF CHROMIUM BY HYDROCHLORIC ACID

Type of Sample	Concentrated HCl Method	Cr in Residue %
18% Cr	10 ml.	3.37, 3.68
	Two 5-ml. portions	2.81, 0.84
	Five 2-ml. portions	0.39
	Six 3-ml. portions	0.12, 0.14, 0.50, 0.32
22% Cr	Six 3-ml. portions, rinse, three 3-ml. portions	0.26, 0.28
27% Cr	Six 3-ml. portions, rinse, three 3-ml. portions	0.28, 0.54

**HYDROCHLORIC ACID TREATMENT AND EFFECT OF HYDROFLUORIC ACID.** The possibility of avoiding the accumulation of large amounts of sodium salts in the solution by the use of concentrated hydrochloric acid in place of sodium chloride was also studied. The method using hydrochloric acid had also been tried by H. H. Willard (18) and by Benedetti-Pichler and Spikes (1). The residual chromium and the methods of addition of hydrochloric acid are tabulated in Table III. Although considerable chromyl chloride was evolved upon the addition of 3 ml. of hydrochloric acid the solution frequently turned green shortly thereafter. The solution was then heated for several minutes until the red

color was restored before adding the next portion of hydrochloric acid. This prolonged heating necessitated adding two or three 10-ml. portions of perchloric acid (70 to 72 per cent) to prevent the solution from being evaporated to dryness. Hydrofluoric acid also causes loss of chromium as a red gas of unknown composition.

Where sodium salts are undesirable, hydrochloric acid in small portions can be used for the elimination of chromium with results comparable to those attained by the use of sodium chloride. The green color noted above is attributed to the formation of trivalent chromium, which is made possible by the cooling effect of the vaporization of the water in the concentrated hydrochloric acid. The time required for reoxidation and the extra perchloric acid necessary make the hydrochloric acid treatment somewhat less desirable than the sodium chloride treatment, except in cases where sodium salts may be objectionable or time is not a factor. If sufficient time can be devoted to an analysis, it is possible to eliminate 99 per cent of the chromium, when concentrated hydrochloric acid is added after repeated oxidations, by heating the perchloric acid solution.

### Effect of Sodium Chloride-Perchloric Acid Treatment on Determination of Other Elements

Since 99 per cent of the chromium can be volatilized, as has been shown above, it remained to determine the effect of this treatment on the analysis of other elements. This investigation was made, therefore, to indicate the analyses in which the volatilization of chromium would be feasible.

With this objective, numerous determinations were made on 20 elements. In general, the procedure followed involved determining the amount of the element in question in known samples with and without the sodium chloride treatment. Standard steels, c. p. metals, c. p. compounds, standard solutions, and Bureau of Standards steels were used as samples. Solution was usually effected by 5 ml. of 6 *N* hydrochloric acid and 15 to 25 ml. of perchloric acid (70 to 72 per cent) for each gram of sample. In many cases, additional control analyses were made, using acids other than perchloric. After the chromium was volatilized, the element being studied was determined in the residue and the controls by the usual methods, modified where necessary by the presence of perchloric acid. Most of the methods were derived from the United States Steel Corporation (19-21) and Hillebrand and Lundell (2-17).

**INTERPRETATION OF RESULTS.** The results of experiments 6 and 7 indicate that the greater part of the tin is volatilized, and experiment 65 shows that this loss is due primarily to the fuming with salt.

Experiments 11, 12, and 58a show a large apparent loss of arsenic. However, experiments 58b and 59 indicate that these tests are not a true measure of the loss, since it is much less if the solution is diluted before reduction or if gravimetric methods are used. Apparently, it is difficult to get all of the arsenic reduced in the presence of perchloric acid. Another possible explanation is that the peroxides which might be formed reoxidize some of the arsenic. In experiments 60 and 62, the loss of arsenic as determined by distillation is 1.5 to 4 per cent.

Experiments 23, 61, and 64 indicate that the sodium chloride-perchloric acid treatment apparently interferes with the reduction of selenium, but no loss is detected by distillation in experiment 63.

Experiment 24 indicates that perchloric acid interferes with the complete precipitation of titanium by cupferron. Experiment 25 shows that if other steel constituents are not removed, they interfere so seriously that color comparison is impossible. Experiment 34, in which potassium dichromate



was added and chromium removed by sodium chloride, indicates that chromium may be volatilized sufficiently to avoid interference with the development of the color. Experiment 36 shows that perchloric acid interferes with the sodium thiosulfate separation also. Undoubtedly, if the perchloric acid were completely reduced, sodium thiosulfate and cupferron separations could be used.

Experiments 44, 45, 57, and 56 indicate that perchloric acid interferes with the phosphate-thiosulfate separation of aluminum, but not with the ammonium hydroxide separation. When phosphorus is present, the aluminum can be separated from the perchloric acid by precipitating with ammonium hydroxide, filtering, and washing. Then the aluminum in the mixed precipitate of  $\text{AlPO}_4$  and  $\text{Al}(\text{OH})_3$  can be dissolved in hydrochloric acid and reprecipitated as phosphate only, by the phosphate-thiosulfate method.

Low results typified by experiment 38 were obtained for tungsten, and  $\text{WO}_3$  continued to precipitate in the filtrates. This phenomenon was attributed to the formation of phosphotungstates, since phosphorus is not removed by perchloric acid, but is removed by hydrochloric acid which is used in the usual solution of the sample. However, by making several recoveries, results were obtained in experiment 43 which indicate that there is no appreciable loss due to salt.

A preliminary experiment indicated that little, if any, iron is lost by sodium chloride-perchloric acid treatment.

The remaining experiments indicate that the perchloric acid-sodium chloride treatment causes no appreciable loss of selenium, aluminum, phosphorus, vanadium, molybdenum, titanium, cobalt, nickel, copper, columbium, zirconium, tungsten, uranium, zinc, beryllium, boron, or sulfur.

**DISCUSSION.** The results and interpretation of these experiments to reveal the effect of the sodium chloride treatment on the determination of the twenty elements listed are of a preliminary nature and should be considered as indicating the course of future investigations with regard to the applicability of this method for separating chromium.

The method described for the determination of manganese in stainless steel has been in use for several months in this laboratory and has proved generally satisfactory. No attempt was made to attain greater precision than that usually expected from the persulfate-arsenite method.

### Summary

A rapid, accurate method for volatilizing chromium prior to the determination of manganese in high-chromium steels is described. Solution of a 1-gram sample is effected by a 4 to 1 mixture of perchloric acid (70 to 72 per cent) and 6 *N* hydrochloric acid. The chromium is volatilized by the addition, in small portions, of 2 to 4 grams of sodium chloride.

TABLE IV. EFFECT OF SODIUM CHLORIDE-PERCHLORIC ACID TREATMENT ON DETERMINATION OF OTHER ELEMENTS

Expt.	Sample and Method	Amount Present %	Amount Found Using <sup>a</sup> Preliminary Treatment				Loss %
			None %	HClO %	HClO and NaCl %		
11 and 12	Arsenic <sup>b</sup>						
	Volumetric (4) (diluted to 70 ml.)	0.2	0.21	0.05	0.05	75	
58a	Gravimetric (3)	0.2	0.13	0.16	0.22	..	
58b	Volumetric (diluted to 70 ml.)	0.2	0.18	0.008	0.011	94	
59	Volumetric (diluted to 350 ml.)	0.2	0.18	0.14	0.14	21	
60	Distillation	0.2	0.18	0.006	0.001	4	
62	Distillation	50	....	0.06	0.70	1.5	
6 and 7	Tin						
	Volumetric (5)	9.5	9.6	9.8	0.69	99	
65	H <sub>2</sub> S precipitate in distillate	100	....	Trace	Large loss		
23	Selenium						
	Volumetric KI-thiosulfate	0.22	0.224	....	0.179	17	
61	Volumetric KI-thiosulfate	0.23	....	0.21	0.13	40	
63	Distillation	0.23	....	Nil	Nil	0	
64	Gravimetric SO <sub>2</sub> reduction	0.23	....	0.17	0.18	20	
41 and 45	Aluminum						
	Phosphate (13)	95	....	90	60	30	
44 and 45	Phosphate (13)	0.37	....	0.10	0.03	90	
57	Phosphate (13)	0.24	....	0.04	0.06	72	
56	NH <sub>4</sub> OH (12)	95	92.4	92.4	95.4	0	
1	Phosphorus						
	Volumetric (19), distillation	0.091	....	....	0.001	0	
21	Volumetric	0.091	....	....	0.096	0	
2	Vanadium						
	Colorimetric distillation	0.165	....	....	Nil	0	
4 and 5	Volumetric	0.05	0.043	0.043	....	..	
6 and 8	Volumetric (9)	0.05	....	0.046	0.043	0	
13	Colorimetric (10)	0.165	0.165	....	0.165	0	
16	Molybdenum, colorimetric	0.39	....	0.39	0.39	0	
41	Columbium, gravimetric	0.48	0.49	0.48	0.51	0	
24	Titanium						
	Colorimetric (21), cupferron	0.496	....	0.23	0.27	..	
36	Colorimetric, thiosulfate	0.496	....	0.27	0.27	..	
25	Colorimetric, Fe present	0.496	Impossible to match colors				
31	Colorimetric, pure solution	0.25	0.25	0.25	0.25	0	
34	Colorimetric, pure solution, Cr added and removed	0.25	0.25	0.25	0.25	0	
29	Nickel, volumetric (6)	9.22	....	9.22	9.22	0	
37	Copper, volumetric (2)	0.30	....	0.30	0.30	0	
39	Cobalt, gravimetric (7)	....	....	0.194	0.197	0	
49	Zirconium, gravimetric (15)	0.12	....	0.12	0.12	0	
38	Tungsten, gravimetric (16)	18.25	....	13.2	15.7	..	
43	Tungsten, gravimetric (16)	2.58	....	2.38	2.36	0	
50	Uranium, gravimetric (11)	47.5	49.00	48.96	49.15	0	
46 and 48	Zinc, gravimetric (8)	95	....	92.9	93.2	0	
52	Boron, gravimetric (17)	21.66	22.1	21.7	22.0	0	
53	Beryllium, gravimetric (14)	11.25	10.8	11.5	11.5	0	
54	Sulfur, gravimetric (20)	....	0.191	0.192	0.194	0	

<sup>a</sup> Apparent losses less than the experimental error are considered nil. In the methods marked "distillation" the gases evolved were absorbed in water and the solution was analyzed for the element being tested.

<sup>b</sup> Control analyses on As contained HClO<sub>4</sub> but were not heated.

The excess chloride is boiled out as hydrochloric acid, and the analysis is finished by the usual persulfate-arsenite method.

A technic has been developed for volatilizing 99 per cent of the chromium from steels containing up to 25 per cent of chromium. This consists of alternate additions of salt in portions to a perchloric acid solution of the steel and of rinsing the sides of the container with distilled water. A similar and equally effective but somewhat longer method of volatilizing chromium has been developed, using small volumes of concentrated hydrochloric acid.

Of the twenty elements tested, the perchloric acid-sodium chloride treatment for volatilizing chromium causes loss of arsenic and tin; interferes with the methods used for the determination of selenium, titanium, aluminum, and tungsten; but does not interfere with the determination of phosphorus, vanadium, molybdenum, cobalt, columbium, nickel, copper, zirconium, uranium, boron, beryllium, or sulfur by the methods used in this investigation.

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# Determination of Acetaldehyde in Wines

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IN CONNECTION with studies on the course of oxidation in wines the authors were interested in the accurate determination of small amounts of aldehyde, of the order of magnitude of 50 mg. per liter, in the presence of sulfur dioxide and the other commonly occurring volatile iodine-reducing substances. Of the available methods (1, 7), the bisulfite and hydroxylamine procedures appeared to offer more possibilities. Therefore the reliability of three modifications of such procedures was investigated, both as to recovery of aldehydes from wines and from pure solutions and also as to the influence of the addition of sulfite.

## Indirect Bisulfite Procedure

In this procedure an excess of bisulfite is added to the solution of aldehyde, the mixture is allowed to stand for the period of time necessary to complete the sulfonic acid formation, and the excess of bisulfite is determined by titration with standard iodine solution. This procedure, apparently first suggested by Ripper (15), has been widely used in the determination of aldehyde by Parkinson and Wagner (13), Valaer (19), Joslyn (8), and others. It has been subjected to a considerable study by Langedijk (10), Kolthoff and Furman (9), Donnally (4), and Parkinson and Wagner (13), and a number of modifications have been suggested. The authors have used a modification based on the suggestions of Kolthoff and Furman (9) to stabilize the bisulfite solution by the addition of 5 to 10 per cent of alcohol and to determine the excess bisulfite by rapidly adding the aldehyde solution to an excess of iodine and back-titrating with standard thiosulfate solution.

Mix 100 cc. of the aldehyde solution, 10 cc. of 0.1 *N* sodium bisulfite solution containing 10 per cent of ethyl alcohol by volume, and 10 cc. of alcohol (if the sample contains none) in a 300-cc. Erlenmeyer flask which is stoppered and allowed to stand at room temperature for 30 minutes. (Aldehyde solutions obtained by distillation were cold when bisulfite was added, so that the solutions were not at room temperature during the whole of the storage period.) Then add 10 cc. of 0.1 *N* iodine solution from a freely flowing pipet, and back-titrate the excess of iodine with 0.1 *N* thiosulfate solution. As a blank, to the same volume of water and alcohol add 10 cc. of the bisulfite solution, stand for 30 minutes, add iodine, and back-titrate as above (1 cc. of 0.1 *N* thiosulfate is equivalent to 0.0022 gram of acetaldehyde).

Kolthoff and Furman (9) report that when about 30 to 50 per cent more bisulfite than is theoretically necessary is added and the mixture is allowed to react for 30 minutes the procedure is very exact even for 0.01 *N* solutions of acetaldehyde and formaldehyde. Ripper (15) had previously reported that 15 minutes are sufficient for 25 cc. of a 0.5 per cent solution of acetaldehyde to which are added 50 cc. of a potassium bisulfite solution containing 12 grams of potassium bisulfite per liter. Parkinson and Wagner (13) used higher concentrations of bisulfite but dealt with stronger aldehyde solutions than did the authors. It is obvious that the presence of sulfur dioxide or other volatile iodine-reducing substances in the wine would interfere with this method.

## Direct Bisulfite Procedures

The quantity of bisulfite bound by the aldehyde is determined by oxidizing the excess of bisulfite with iodine under conditions such that the aldehyde-bisulfite complex is not dissociated, then hydrolyzing the latter, and titrating the sulfite liberated with standard iodine solutions. Although, according to Jaulmes and Espezel (7), such a procedure was suggested as early as 1896 by Reiter, the rational development of the most suitable conditions for the reactions involved depended upon such studies of the chemistry of these reactions as were made early by Kerp (9) and later by Stewart and Donnally (16) and Jaulmes and Espezel (7). Although a number of procedures of this kind are now available (Clausen, 3, Friedemann and Kendall, 6, Friedemann and Graeser, 5, Tomoda, 17, Donnally, 4, and Jaulmes and Espezel, 7) the latter procedure has been selected because it was developed for conditions that are found in wine distillates.

Place 100 cc. of aldehyde solution (containing between 0.01 and 0.03 gram of acetaldehyde) in a 500-cc. Erlenmeyer flask, and add 50 cc. of neutral buffer solution (3.35 grams of  $\text{KH}_2\text{PO}_4$  and 15 grams  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  per liter, or 24 grams of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 25 cc. of *N* sulfuric acid per liter) and 10 cc. of bisulfite solution (18.9 grams of anhydrous sodium sulfite and 150 cc. of *N* sulfuric acid per liter). Stopper, shake, and let stand 20 minutes. Add 1 cc. of freshly prepared 0.2 per cent starch solution, 100 cc. of water, and 10 cc. of acid solution (250 cc. of concentrated hydrochloric acid, 22° Bé., per liter). Then titrate the excess bisulfite with 0.1 *N* iodine solution. Add 100 cc. of alka-



line solution (8.75 grams of boric acid and 400 cc. of *N* sodium hydroxide per liter) and titrate again with 0.1 *N* iodine to determine the liberated sulfite.

### Hydroxylamine Procedure

The reaction of aldehydes with hydroxylamine hydrochloride to form the aldoxime, with the liberation of the equivalent amount of acid which may be determined by titration with alkali, has been widely used for the determination of aldehydes and ketones, particularly those of high molecular weight found in essential oils (11, 12, 14) and its use has been suggested for determination of aldehydes in wine by Charles (2).

TABLE I. RECOVERY OF ALDEHYDES IN PURE ALDEHYDE SOLUTIONS<sup>a</sup>

Acetaldehyde Added <i>P. p. m.</i>	Hydroxylamine		Indirect Bisulfite	
	<i>P. p. m.</i>	%	<i>P. p. m.</i>	%
9.8	8.2	84	7.5	77
19.5	19.1	98	18.6	96
39.0	35.9	92	35.9	92
97.6	91.6	94	84.1	86
195.1	181.4	93	179.8	92
390.2	351.1	90	338.1	87

<sup>a</sup> In very dilute solutions the error in titration is large enough to account for the apparently low recoveries.

In the Charles procedure the aldehyde solution is neutralized to methyl orange, an excess of 0.5 *N* hydroxylamine hydrochloride solution is also neutralized to methyl orange, and the acidity produced in the reaction is determined by neutralization with 0.2 *N* sodium hydroxide. In the Leone and Tafuri (11) procedure the aldehyde solution is added to a solution of hydroxylamine hydrochloride, the  $\text{NH}_2\text{OH}$  of which is set free by neutralization with sodium hydroxide to a phenolphthalein end point. Then the excess hydroxylamine present is determined by titration with acid to a methyl orange end point. The aldehyde is calculated from the difference between this titration and the titration of the original hydroxylamine hydrochloride solution to a phenolphthalein end point.

Palfray and Tallard (12) recommended the use of bromophenol blue as indicator in place of methyl orange, to minimize errors in the procedure caused by the presence of organic acids. The authors have found the bromophenol blue indicator preferable, also, because of the sharpness of the color change which can be accentuated by titrating with artificial light, the color changing sharply from yellow in acid solution to pink in basic solution.

TABLE II. RECOVERY OF ALDEHYDES FROM PURE SOLUTIONS

Aldehyde Present <i>P. p. m.</i>	Recovery		
	Hydroxylamine %	Indirect bisulfite %	Direct bisulfite %
Direct Titration			
7.9	70 <sup>a</sup>	76 <sup>a</sup>	79 <sup>a</sup>
39.4	85 <sup>a</sup>	86	87
81.0	88	89	87
162.0	89	89	87
324.0	89 <sup>b</sup>	89 <sup>c</sup>	89 <sup>c</sup>
Distillation and Titration			
7.9	89 <sup>d</sup>	86 <sup>d</sup>	94 <sup>d</sup>
39.5	86	89	86
79.0	89	87	86
158.1	87	88	89

<sup>a</sup> 250-cc. sample distilled.

<sup>b</sup> 50-cc. sample distilled.

<sup>c</sup> 25-cc. sample distilled.

<sup>d</sup> 200-cc. sample distilled.

An aliquot of the aldehyde solution (100 cc.) is neutralized with 0.1 *N* sodium hydroxide to the bromophenol blue end point, 5 cc. of neutralized 0.5 *N* hydroxylamine hydrochloride solution are added, and the mixture is allowed to stand for 30 minutes. [At room temperature the reaction is practically instantaneous and the solution need not be allowed to stand; but in the cold (about 0° to 10° C.) the reaction is so slow that it is necessary to allow time for more complete recovery.] Then the acid liberated is titrated with 0.1 *N* sodium hydroxide (1 cc. of 0.1 *N* sodium hydroxide is equivalent to 0.0044 gram of acetaldehyde).

### Preparation of Solutions

The aldehyde solutions were prepared at first by dilution of acetaldehyde-ammonia as directed by the Association of Official Agricultural Chemists (1) but in water and not in alcohol solutions. In subsequent tests the aldehyde was added as such from a stock solution prepared by redistillation of analytical reagent grade acetaldehyde. The redistilled aldehyde was stored at 0° C. and the solutions used were prepared by pipetting known volumes at 0° C., assuming its specific gravity at 0° C. to be 0.806. The determinations were made on 100-cc. aliquots of the aldehyde solution as such and also after distillation. The aldehyde was recovered by mixing 100 cc. of the solution with 50 cc. of water, distilling directly, and collecting about 100 cc. of the distillate in an Erlenmeyer flask immersed in ice water. No mercury trap was used as advised in the official procedure (1) and the volume distilled was larger. In the official procedure 100 cc. of spirit with 12.5 cc. (formerly 50 cc. of water were used) of added water are distilled and about 100 cc. of distillate are collected.

No study was made of the aldehyde recovery by distillation, but the data indicate a fairly complete recovery. Following the suggestion of Trillat (18) the sample was acidified with 20 cc. of a 5 per cent phosphoric acid solution to dissociate combined aldehyde. The distillate from wines was prepared in the same manner. The determinations were made in duplicate and if duplicates did not agree closely they were repeated. Using a 10-cc. buret it was found possible to get duplicate determinates agreeing usually to less than  $\pm 0.02$  cc., the largest deviation being  $\pm 0.05$  cc. on wine distillates. In very dilute solutions the error in titration is large enough to account for the apparently low recoveries.

The results are expressed as milligrams of aldehyde per liter of sample, and the recovery obtained under various conditions is shown in Tables I to V.

The recovery of aldehyde in solutions prepared from pure aldehyde ammonia by the hydroxylamine and the indirect bisulfite procedure is shown in Table I. The hydroxylamine procedure gives recoveries that are slightly higher than by the indirect bisulfite procedure, although the recovery by both procedures is low for dilute solutions and for the more concentrated solutions.

TABLE III. RECOVERY OF ALDEHYDES IN PRESENCE OF 12 PER CENT ALCOHOL

Aldehyde Present <i>Mg./l.</i>	Recovery		
	Hydroxylamine %	Indirect bisulfite %	Direct bisulfite %
Direct Titration			
7.9	75 <sup>a</sup>	85	96
39.4	86	83	89
78.8	87	83	87
81.0	89	83	88
157.6	87 <sup>b</sup>	79 <sup>b</sup>	86 <sup>b</sup>
162.0	87	87	88
315.2	88 <sup>b</sup>	79 <sup>c</sup>	87 <sup>c</sup>
Distillation and Titration			
7.9	87 <sup>d</sup>	80 <sup>d</sup>	92 <sup>d</sup>
39.5	88	88	92
79.0	89	85	91
158.1	89	71	91

<sup>a</sup> 250-cc. sample distilled.

<sup>b</sup> 50-cc. sample distilled.

<sup>c</sup> 25-cc. sample distilled.

<sup>d</sup> 200-cc. sample distilled.

The recovery of aldehydes from solutions prepared from redistilled aldehyde is shown in Table II both by direct titration and by distillation before titration. Little loss of aldehyde occurred during distillation even in the more dilute solutions. There is also but little difference between the recoveries obtained by the various methods.

The recovery in the presence of added alcohol is shown in Table III. The alcohol significantly decreased the recovery by the indirect bisulfite procedure. Jaulmes and Espezel (7) pointed out that alcohol reduced the rate at which the aldehyde combines with bisulfite, but according to the data they present the retardation, although apparent at 10 per



TABLE IV. RECOVERY OF ALDEHYDES IN PRESENCE OF 12 PER CENT ALCOHOL AND ADDED SULFITE

Aldehyde Present <i>Mg./l.</i>	SO <sub>2</sub> Present <i>Mg./l.</i>	Recovery		
		Hydroxylamine %	Indirect bisulfite %	Direct bisulfite %
		Distillation and Titration		
39.5	0	88	88	92
	25	80	51	93
	100	64	None	93
158.1	0	89	71	91
	25	81	60	90
	100	70	39	90

cent alcohol, is not very marked until about 40 or 50 per cent of alcohol is present. To check this point 100-cc. portions of aldehyde solution containing 79.05 mg. per liter of acetaldehyde and 12 per cent by volume of alcohol were mixed

recovered by the direct bisulfite procedure and least recovered by the indirect bisulfite procedures.

## Summary and Conclusions

A modified Ripper procedure, a modified hydroxylamine procedure, and the Jaulmes and Espezel procedure of determining aldehydes were compared. In pure acetaldehyde solutions the three procedures gave comparable results. In the presence of 12 per cent of alcohol (added as 95 per cent grain alcohol) the recovery by the modified Ripper procedure was reduced, although it could be increased by increasing the reaction time. In the presence of sulfites only the Jaulmes and Espezel procedure gave fairly complete recovery. However, in no case was the recovery as complete as reported for higher concentrations of aldehyde.

TABLE V. RECOVERY OF ALDEHYDES FROM WINE

Wine	Type	Remarks	Hydroxylamine	Aldehyde Content	Direct bisulfite
			Mg./l.	Indirect bisulfite Mg./l.	Mg./l.
1	Sherry	Commercial	109.2	74.6 (0.5 hr.)	116.6
2	Sherry	Experimental	93.4	94.6 (1 hr.)	
3	Sherry	(3-5-5)		67.1 (0.5 hr.)	96.7
4	Burgundy	Experimental	202.5	86.9 (1 hr.)	
5	Sherry	(5-7-3)		122.5 (0.5 hr.)	215.3
6	Burgundy	Eastern	46.7	150.5 (1 hr.)	
7	Sherry	Experimental	154.5	37.6 (1 hr.)	53.6
8	Fermented mut�	Contains about	222.2	36.5 (1.5 hr.)	
9	Claret	1000 p. p. m. of		128.3 (1 hr.)	170.8
10	Muscat	SO <sub>2</sub>		129.8 (1.5 hr.)	
11	Port	Commercial		No recovery	666.2
12	Dry white	Commercial	129.0 <sup>a</sup>	70.1	80.2
13	Sherry	Commercial	52.6	54.6	52.5
14	With 63.2 p. p. m. added acetaldehyde		85.7	No recovery	112.8
15	With 63.2 p. p. m. added acetaldehyde		31.7	26.1	37.6
16	With 63.2 p. p. m. added acetaldehyde		51.7	51.0	53.7
17	With 63.2 p. p. m. added acetaldehyde		131.2	26.8	170.9
18	With 63.2 p. p. m. added acetaldehyde		(72% recovery)		(92% recovery)
19	With 63.2 p. p. m. added acetaldehyde		83.4	79.5	94.4
20	With 63.2 p. p. m. added acetaldehyde		(82% recovery)	(85% recovery)	(90% recovery)
21	With 63.2 p. p. m. added acetaldehyde		104.7	96.4	111.6
22	With 63.2 p. p. m. added acetaldehyde		(84% recovery)	(72% recovery)	(92% recovery)

<sup>a</sup> Result of single observation.

with bisulfite and titrated in duplicate after 30 and 60 minutes, respectively. After 30 minutes of standing only 76 per cent of the aldehyde present was recovered; after 60 minutes, 88 per cent. Further standing did not appreciably increase aldehyde recovery.

The effect of added sulfite is shown in Table IV. The aldehyde solutions were prepared with sufficient bisulfite added to give 25 and 100 p. p. m. of available sulfur dioxide, and with 12 per cent of alcohol. They were distilled after addition of 20 cc. of 5 per cent phosphoric acid to 100 cc. of sample and 50 cc. of water. The presence of sulfur dioxide markedly reduced the recovery by the indirect bisulfite procedure, noticeably reduced that by the hydroxylamine procedure, but had little effect on the direct bisulfite procedure, as was to be expected.

A number of samples of wine were analyzed for their aldehyde content by the three procedures, with the results shown in Table V. With two exceptions (wines 8 and 11) the indirect bisulfite procedure, even with an increased reaction time gave low results. Higher results were obtained with the hydroxylamine procedure, but in general these were not as high as by the direct bisulfite procedure. In the case of wine 9 a surprisingly high result was obtained by the direct bisulfite procedure. Acetaldehyde added to wine was not completely

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# Complete Removal of Ferric Chloride from Solution

## By a Continuous Extraction with Ether

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**A** LONG-STANDING difficulty in the analysis of ferrous alloys is the separation of iron which is necessary before many constituents of the dissolved sample can be determined. The smaller the amount of material that is present, the larger must be the sample which is taken for analysis, the more serious is the interference, and the greater the quantity of iron that must be separated from the solution. This problem leads to the technic described in the present paper.

Of several possible procedures which have been developed heretofore to achieve this purpose, the well-known method (5, 6) employing a diethyl ether extraction seemed to provide the greatest speed and capacity. Unfortunately the manual extraction of the ferric chloride with diethyl ether is so inconvenient that for most purposes it is not feasible to reduce the amount of iron beyond 5 per cent of that originally present, though it is reported that the iron may be reduced to "a few tenths of a milligram" (3). Theoretically there appeared to be no reason why the separation of ether might not be made

complete, unless there were a reaction between the ferric chloride and ether solution. Furthermore, ferric chloride is not volatile with ether (7). The efficiency of the process might be low toward its end, but this should not prove an obstacle if the process were made mechanical and continuous.

Of several forms of apparatus already available for this purpose, that represented in Figure 1 (as supplied by the Scientific Glass Apparatus Co., Bloomfield, N. J.) appeared to be best suited to the quantitative handling of a solution. Preliminary tests made with pure ferric chloride solutions gave complete separation, but, when samples prepared from actual steels were run, the separation was very poor. A large portion of the iron was reduced to the ferrous condition and of course not removed by the ether. The paper by Dodson, Forney, and Swift (1) suggested that the substitution of diisopropyl ether might prevent this reduction, but the action appeared to be about the same. The mention (4) by McNaught of a successful continuous extraction by diethyl ether led the authors to believe that the results with pure ferric chloride solutions could be repeated if the cause of the iron reduction were discovered. Careful purification of both ethers failed to improve results. The addition of oxidizing agents proved impractical. A search of the literature for possible "catalysts" failed to reveal anything to account for this reducing action. However, it has been established that ferric chloride in ethereal solution does undergo photochemical reduction (2), and this proved to be the cause of the difficulty.

A series of extractions was then run in the dark. It was found that no iron was reduced and the extractions were to all intents complete. Reference to the authors' initial successful tests showed that they had been run overnight and were as a consequence protected from strong light; all the later unsuccessful runs had been made in diffuse daylight.

### Procedure

A 10-gram sample of iron is put into solution, and the silica and other insoluble material are removed. The iron is converted to the chloride and taken to dryness. An oxidizing agent should be used to destroy ferrous chloride. The sample is transferred to the extraction apparatus with 100 ml. of 8 to 9 *N* hydrochloric acid, the apparatus is set up with 200 ml. of diisopropyl ether in the flask, and the ether is set to boil. The vapors condense to a liquid which falls through the funnel and escapes at the bottom of the extraction vessel. The droplets make their way to the surface of the ferric chloride solution and, saturated with ferric chloride, finally spill over into the flask.

When very large amounts of iron are being removed, it may be necessary to replace the diisopropyl ether after about an hour in order to reduce foaming. Beads (or, better, silicon carbide chips) are added to reduce bumping. The operation is complete in 16 hours (overnight), but all but a minute amount of iron is probably out at the end of 8 hours. The process is carried out in weak artificial light or in darkness.

No test for iron could be obtained in the residues from overnight extraction with either potassium thiocyanate (after oxidation) or with thioglycollic acid in ammoniacal solution. However, a spectrographic examination of the cupferron precipitate from the residue revealed a minute trace of iron.

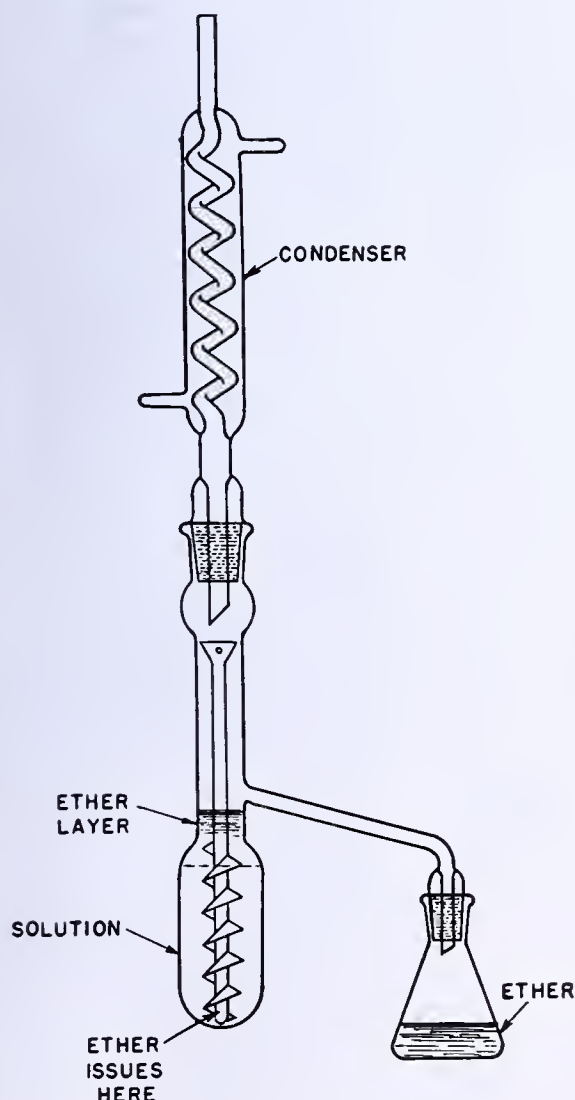


FIGURE 1. DIAGRAM OF APPARATUS



To determine whether this continuous extraction was removing an appreciable amount of other elements which are not customarily removed by the ether extraction, a solution containing 10 mg. of copper per 1000 ml. was extracted for 16 hours. The diisopropyl ether extract was evaporated to dryness and the residue tested with ammonia and sodium diethyldithiocarbamate. No trace of copper was found.

This method allows a considerable economy in the amount of ether required for the extraction.

### Summary

Iron may be completely separated from an aqueous solution as the chloride by a continuous extraction with ether in the dark.

The method is convenient and allows a considerable saving in the amount of ether required for the extraction.

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# Determining the Corrosion Resistance of Tin Plate

## The Hydrogen Evolution Test

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TIN cans have a commercial record of many years' standing as satisfactory containers for fruits and fruit products. However, acid corrosion of the tin plate by fruits (and even by some vegetables) has always confronted the industry and results in losses due to perforation of the tin plate or the formation of "hydrogen swells," a term denoting a puffed condition in the can caused by an accumulation of hydrogen. In some years these losses have constituted a very serious economic problem, especially when large portions of the pack have been carried over into the second season.

To alleviate these losses numerous investigators have studied the subaqueous corrosion of tin plate and have explained, in part, the mechanics of the corrosion of tin plate by fruit acids. During recent years, the International Tin Research and Development Council under the direction of D. J. McNaughton has published several papers (4, 5, 6) which bring this knowledge up to date. This organization has built upon the foundation laid by Evans (2), Mantell (10), Lueck and Blair (9), Kohman and Sanborn (8), Morris and Bryan (11), Culpepper and Moon (1), and many others.

An excellent monograph on tin-can corrosion has been prepared by Hirst and Adam (3).

The investigators have explained that the tin coating protects the steel base of the tin plate electrochemically, because tin is anodic to steel in most food acids. (The references cited show that the relative potentials of the  $\text{Fe}:\text{Fe}^{++}$  and  $\text{Sn}:\text{Sn}^{++}$  half cells have little to do with the electrochemistry of tin and iron in a can of an acid food product.) Previous workers have also shown that many materials act as powerful accelerators of corrosion. They have studied the effect of packing variables and storage conditions on service life and have shown that different lots of tin plate vary considerably in rates of corrosion in acids.

These investigations indicate that the fruit packer may lengthen the average service of his cans in the following ways:

1. By use of cans made of so-called type L, or low metalloid cold reduced steel.
2. By use of cans made of tin plate carrying heavier tin coat-

ings. This is often uneconomical because of the increased cost of the containers.

3. In some cases by adequate washing of the raw fruit to eliminate spray residues and by use of sulfur-free sugar for sirups.

4. By reducing the oxygen content of the can by "exhausting" the can, either thermally or mechanically.

5. By maintaining a reasonable head space in the can. This provides a hydrogen "reservoir."

6. By cooling the cans with water after processing.

7. By storing the cans at cool temperatures. This is not always possible and is frequently costly.

In spite of the improvements in canning technic, the canning industry has been troubled with excessive losses due to the early appearance of hydrogen swells which could not be explained on the basis of poor cannery practice, poor can manufacture, or poor can closure. These more or less sporadic cases of short service life have been traced to tin plate having a low resistance to acid corrosion. Unless the small percentage of tin plate responsible for early hydrogen springer formation can be eliminated, fruit packers will continue to be confronted with corrosion losses.

The need for a simple corrosion test that will permit reasonably accurate predictions of can service life and can be applied to commercial shipments of tin plate is obvious. Such a test, based on the rate of hydrogen evolution, under standard conditions, from formed samples of tin plate, was devised in 1932 to measure the difference in corrosion resistance of various lots of tin plate and is the subject of this paper. It has been used satisfactorily as a routine control test of commercial shipments of tin plate since that time.

An accelerated corrosion test, in which one or more of the factors affecting corrosion has been intensified, cannot be safely used to predict "can service value" under commercial conditions until the test values have been definitely correlated with the actual commercial service values. The accelerated corrosion test devised in these laboratories (the "hydrogen evolution test") has been proved by many thousands of correlating tests with plain (unlacquered) cans packed with such products as peaches, pears, Royal Anne cherries, and dried prunes in sirup, so that it is possible to predict with reasonable accuracy the service life to be expected from a



tested lot of tin plate when made into cans and packed with these products. These correlations are described below.

### Definition of Terms

**HYDROGEN EVOLUTION VALUE.** "Hydrogen evolution value" is a measure of the corrosion resistance of a tin-plate specimen subjected to the hydrogen evolution test and is defined as the time in hours required to produce 5 cc. of gas by the action of *N* hydrochloric acid on a die-formed specimen of tin plate in the apparatus and under the conditions described below.

TABLE I. HYDROGEN EVOLUTION VALUE

Sheet No.	Samples Tested per Sheet		Average Hydrogen Evolution Value		Difference	
	Die-formed	Flat disk	Die-formed Hours	Flat disk Hours	Hours	%
1	19	21	19.3	51.9	32.6	169
2	19	21	23.0	48.2	25.2	110
3	18	17	36.7	52.9	16.2	44.1
4	24	21	48.8	68.8	20.0	41.0
5	24	21	52.9	69.6	16.7	31.6

**CAN SERVICE VALUE.** For the purposes of this paper, "can service value" of tin plate with respect to a given food product is a measure of the resistance to corrosion losses of a set of cans made from any one lot of tin plate. Plain cans, size 2 $\frac{1}{2}$ , are made from a given lot of tin plate, packed with the food product, and stored at 37.78° C. (100° F.). Sets of 50 to 100 cans are thus prepared and stored and the time in months required for 50 per cent of the cans to swell because of hydrogen pressure is defined as the can service value.

### Apparatus

The corrosion cell, shown in Figure 1, consists of an open-bottom, glass bell-shaped unit, *A*, of 500-cc. capacity, provided with a ground-glass flange to which is clamped the test specimen, *E*, which is formed with a die having the same profile as used on a standard sanitary can end (6.7-cm., 2 $\frac{1}{16}$ -inch diameter). Special rubber gaskets, *X*, form the seal between the glass unit and specimen and between floating ring *b* and flange of glass vessel *A*.

The bronze base, *B*, consists of three parts—*c*, a threaded disk countersunk to take the sample; *b*, a floating ring over a rubber gasket on the glass flange; and over this a threaded ring, *a*, which screws onto disk *c* and clamps the whole unit together. *Z* is a spanner wrench fastened to a table. An olive-tip gas eudiometer, sealed at the top by means of a glass plug, *G*, is attached to the glass unit, *A*, as indicated, to collect evolved gas. Overflow tube *D* is a reservoir for acid displaced by the gas evolved by corrosion.

The apparatus is similar in principle to that described in 1936 by Morris (11). The essential difference is that Morris tested flat disk specimens, whereas the specimens used in the above apparatus are die-formed as in commercial use.

The necessity for using die-formed test specimens rather than flat disk specimens to measure the acid corrosion resistance of tin plate is apparent from examination of hydrogen springers in commercial fruit packs and of hydrogen evolution values on die-formed specimens compared with hydrogen evolution values on flat disk specimens.

Examination of thousands of hydrogen springer cans of commercial fruit packs has shown that corrosion responsible for

hydrogen springers and perforations is usually localized on the ends, especially at the areas where the drawing strain is greatest. This is particularly true of the end stored down, which is in intimate contact with the can's contents. The plate in the cylindrical body of the can, except at the double bend at the side seam where the metal has been strained, is not usually corroded to the same degree. Stamping and bending the tin plate result in an increase in porosity (7) and also cause fractures in the tin coating.

Hydrogen evolution values with die-formed specimens are lower than those obtained with flat disk samples of any given lot of plate. Furthermore, the percentage difference is larger on plate of low corrosion resistance than on plate of high corrosion resistance. In other words, hydrogen evolution values on die-formed samples evaluate tin plate more satisfactorily with respect to corrosion resistance than do hydrogen evolution values on flat disk samples. This is illustrated in Table I.

### Corrosion Medium

The corrosion medium is 1.000 *N* c. p. hydrochloric acid. This is stored at 48.9° C. (120° F.) in vented 20-liter (5-gallon) bottles for 96 hours to assure equilibrium with reference to dissolved air content.

Hydrochloric acid was adopted for the corrosion medium in order to obtain more rapid corrosion, so that routine tests could be completed in a reasonably short time. Citric acid behaves like hydrochloric, but the corrosion rate is very much slower.

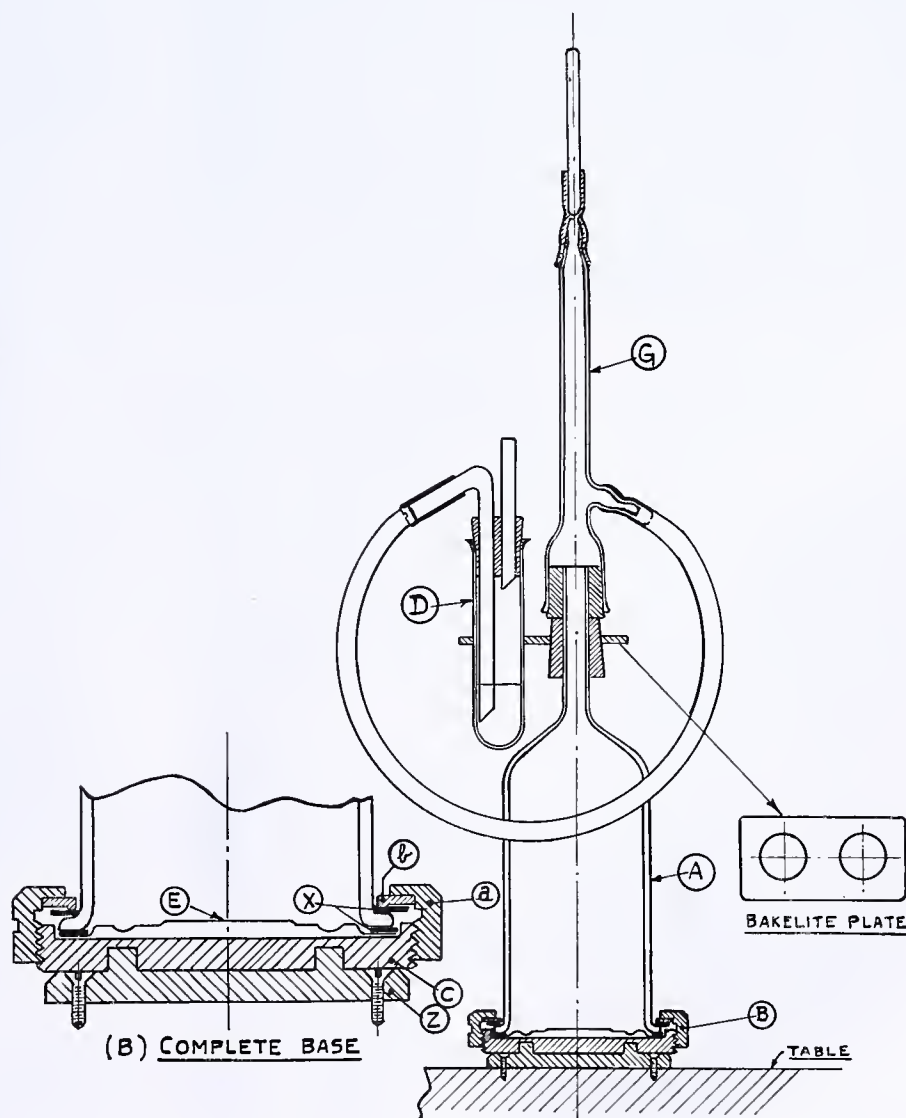


FIGURE 1. COMPLETE HYDROGEN EVOLUTION TEST UNIT



## Procedure

The assembled units are filled with acid by gravity flow through the overflow tube shown in Figure 1. The glass plug in the Bunsen valve at the top of the eudiometer is removed to permit displaced air to escape during filling. Acid flow during filling is adjusted to permit free escape of displaced air from the unit.

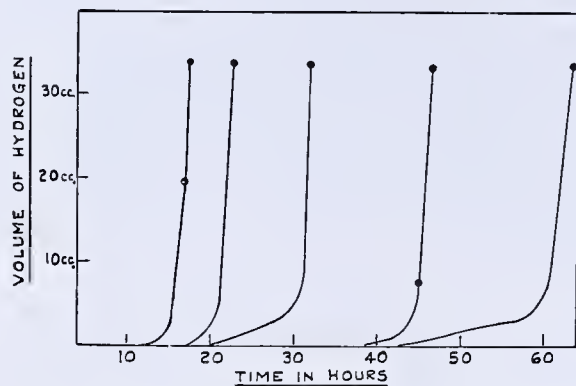


FIGURE 2. TYPICAL HYDROGEN EVOLUTION CURVES

The filled units are placed to a depth of 14.375 cm. (5.75 inches) in a constant-temperature bath at 57.22° C. (135° F.). A 0.3-cm. (0.125-inch) film of crystal oil over the water aids in maintaining the temperature by decreasing the amount of evaporation. The room temperature is maintained at 48.9° C. (120° F.), giving a differential in temperature between the eudiometer and the glass base sufficient to provide a gentle agitation of the corroding medium by convection currents. This was found to be necessary to assure uniform results. When tests were conducted in a room with no differential in temperature between buret and glass base, the rate of corrosion was slower than when a temperature differential was maintained. A room temperature of 48.9° C. (120° F.) was designated because of the impracticability of maintaining lower temperatures throughout the year in all laboratories which were using the hydrogen evolution test.

**PRECAUTIONS.** All glass ware is thoroughly cleaned with water.

Rubber parts including gaskets are desulfurized by boiling in 5 per cent sodium hydroxide for 1 hour, followed by thorough rinsing and subsequent boiling for 10 minutes in *N* hydrochloric acid to remove traces of caustic. They are then rinsed and stored under distilled water until used. Fresh gaskets are treated each day and no gaskets which have been held under distilled water for more than 24 hours after treatment are used.

Test specimens are thoroughly cleaned of palm oil and dust with suitable solvents—chloroform, ethyl acetate, and the like—followed by a light buffing with a clean, soft cloth. The glass unit is clamped to the metal base with the maximum possible screw pressure.

Assembled units are tested for leaks with 258 mm. (5 pounds) air pressure prior to filling.

Filled units are kept in the constant-temperature bath at 57.22 ± 0.27° C. (135 ± 0.5° F.) until 5 cc. of gas have evolved. Volume measurements are made at 2-hour intervals. In routine tests correction of gas volumes to normal temperature and pressure is unnecessary.

The following points of technic must be adhered to closely in order to obtain significant values:

**TEMPERATURE.** The temperature of the water bath is maintained at 57.22 ± 0.27° C. (135 ± 0.5° F.) by means of a suitable thermoregulator. The bath is enclosed in a constant-temperature room controlled to 48.9 ± 0.6° C. (120 ± 1.0° F.).

**NORMALITY OF ACID.** Variation of 0.2 per cent in concentration does not cause noticeable variations in corrosion rate.

**RUBBER GASKETS.** The accelerating effect of sulfur is well known and precautions are taken to desulfurize all gaskets just prior to using. The standardized procedure for this is described above.

Early in the development of the test it was discovered that different types of rubber produced different rates of corrosion on adjacent test specimens cut from the same sheet of plate. To eliminate this variable, a special rubber formula was developed for the gaskets. Since the composition of the gaskets is such an important factor, standardized gaskets from only one source are used. (At present, special standardized hydrogen evolution gaskets are distributed by Wilkens-Anderson Co., Chicago, Ill.)

**OXYGEN CONTENT OF ACID.** Since it was found impractical to eliminate the dissolved air completely from the corrosion medium, the oxygen content is controlled by maintaining a constant elevated storage temperature. The acid is stored at 48.9° C. (120° F.) in 20-liter (5-gallon) bottles which are vented for 96 hours and then stoppered. This procedure controls the dissolved air content satisfactorily.

**QUALITY OF WATER USED TO MAKE UP THE ACID.** Triple-distilled water has been adopted because single-distilled water from many sources contains minute quantities of some unknown accelerating agent.

**VIBRATION OF UNITS DURING TEST.** The corrosion rate can be increased by continuous vibration which loosens the small bubbles of hydrogen forming on the cathodic surfaces. Vibration is kept to a minimum with the aid of rubber hose couplings to the circulating pump and shock absorbers on the constant-temperature bath.

## Typical Results

Typical hydrogen evolution curves are shown in Figure 2.

An induction period, during which gas is evolved very slowly although tin is going into solution, is followed by a sudden change in slope when the rate of hydrogen production is materially increased. This change in slope usually takes place when about 5 cc. of hydrogen have been evolved. The better the tin plate from a corrosion-resistance standpoint, the longer is the induction period. It is during this period that the tin is giving its protection to the base steel.

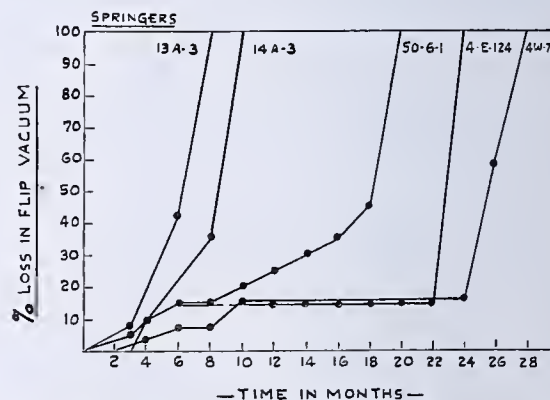


FIGURE 3. TYPICAL VACUUM LOSS CURVES

Individual No. 2½ cans of peaches, stored at 37.78° C. (100° F.)

From the above it is apparent that the 5-cc. value is a critical one, representing the beginning of rapid corrosion of the plate, and it therefore becomes the base on which the hydrogen evolution test is established.

Most cans packed with California fruits show the same type of behavior. There is a period of induction with a fairly small vacuum loss as indicated by "flip" vacuum tests, followed by rapid loss in vacuum and shortly afterward by enough internal pressure to make the can a "springer" or a "swell" (Figure 3). (The "flip" vacuum is the external vacuum necessary to cause the end to snap out. This is measured by means of a device consisting of a shallow chamber, which can be fitted snugly to the top of a can and evacuated with a pump. The chamber is fitted with a suitable vacuum gage and release valve.)



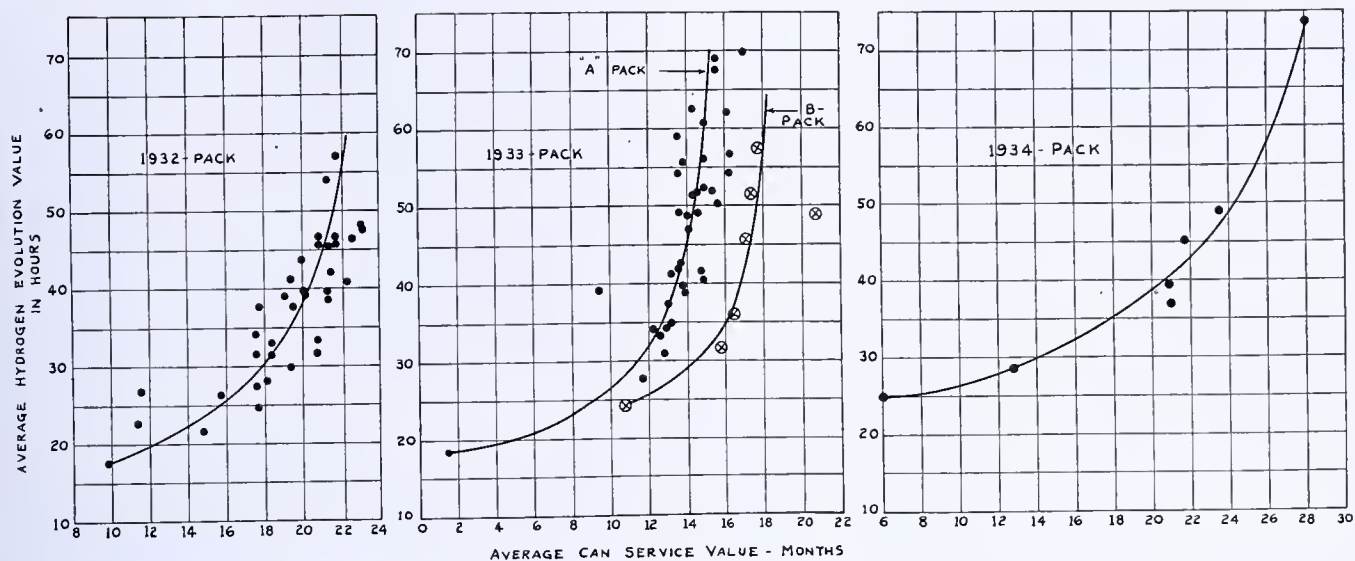


FIGURE 4. CORRELATION OF CAN SERVICE AND HYDROGEN EVOLUTION VALUES FOR PEACHES

TABLE II. CAN SERVICE VALUE AT DIFFERENT STORAGE TEMPERATURES

Product	Type of Can	Can Service Value			
		37.78° C. (100° F.)	26.67° C. (80° F.)	15.56° C. (60° F.)	21.11° C. (70° F.) <sup>a</sup>
Commercial Cans					
Peaches	Plain	1.0	1.7	...	...
Royal Anne cherries	Plain	1.0	2.0	2.0	...
Apricots	Plain	1.0	2.0	...	...
Grapefruit	Plain	1.0	...	7.8	...
Prunes in sirup	Plain	1.0	...	...	2.1 <sup>a</sup>
Strawberries	Enameled	1.0	1.5	3.8	...
Loganberries	Enameled	1.0	1.8	3.6	...
Cans from Plate of Known Corrosion Resistance					
Dried prunes in sirup					
Less than 35 hours	Hot rolled	1.0	...	...	1.6 <sup>b</sup>
More than 35 hours	Hot rolled	1.0	...	...	2.3 <sup>b</sup>
More than 47 hours	Type L	1.0	...	...	4.0 <sup>b</sup>
<sup>a</sup> California warehouse, mean temperature 21.11° C. (70° F.).					
<sup>b</sup> American Can Co. data. The other figures are unpublished data of the Western Branch Laboratory of the National Cannery Association supplied by the courtesy of G. S. Bohart.					

<sup>a</sup> California warehouse, mean temperature 21.11° C. (70° F.).

<sup>b</sup> American Can Co. data. The other figures are unpublished data of the Western Branch Laboratory of the National Cannery Association supplied by the courtesy of G. S. Bohart.

Determination of Can Service Value

The following outline briefly summarizes the steps followed in making the different experimental packs:

1. The tin plate is sorted into lots according to steel manufacturing and composition variables, and each sheet is marked with a suitable code identifying the lot and individual sheet. This code is applied in such a manner that it appears on each part—that is, top, bottom, and body—of each can made from that sheet.

2. The tin plate is made into cans in sets, one sheet of plate from each lot comprising a set. Thus, if ten lots of tin plate were being studied, each set would contain one can from each lot. The sequence of the cans in the sets themselves is carried through all can-manufacturing, can-packing, and can-closing operations, so that the influence of any manufacturing or canning variables will be the same on each lot. Manufacturing operations are under constant supervision, so that the finished can will consist entirely of plate from the same original sheet. This eliminates the sheet-to-sheet variations found in tin plate.

3. No. 2½ cans 11.6 × 12.7 cm. (4⅛ × 4⅞ inches) have been used for two reasons: The bulk of commercial packs of California fruits is in this size, and the No. 2½ can is best adapted to the flip vacuum test for studying the loss in vacuum by hydrogen formation.

4. The cans are packed in a commercial cannery in sets in the same sequence in which they are manufactured. This procedure distributes any fruit or canning variables equally among all lots. Constant vigilance is required to keep the cans in the proper sequence, so that when they are closed the code on the can cover coincides with that on the can body.

5. The completed pack is then transferred to the laboratory for observation. The cans are stored in cases in the same sequence as used in manufacturing and packing, so that small variations in storage temperature will be manifest equally in all lots. The cases are stored in a thermally regulated room and are inspected periodically for vacuum loss or springer formation.

In all the correlating experiments with plain cans described in this paper, a storage temperature of 37.78° C. (100° F.) was maintained. This temperature is not above the commercial range, since products shipped to tropical countries are subjected to similar storage conditions and the temperatures in some California warehouses exceed 37.78° C. (100° F.) during the summer months. Storage at 37.78° C. (100° F.) results in shorter service value than storage at lower temperatures. Usually service value at 37.78° C. (100° F.) continuous storage is about half of that at 26.67° C. (80° F.) continuous storage. Recent data indicate that the corrosion resistance (as measured by the hydrogen evolution test) affects the ratio of can service value at 37.78° C. (100° F.) storage to that at 21.11° C. (70° F.) storage. Table II shows the effect of temperature on service value. The cans held at 37.78° C. (100° F.) have been assigned the service value 1.0 and the service value at the other temperatures is rated accordingly.

Can Service Value-Hydrogen Evolution Value Correlations

The residues from each sheet corresponding to each can in the experimental pack are hydrogen evolution tested. One sample from each sheet was taken for the correlations described below. Experience has shown that, for the practical application of the test, one sample per sheet is adequate because the effect of intrasheet variation is minimized when a sufficiently large number of sheets is tested.

Figures 4 to 8, inclusive, are correlations of average can service value with average hydrogen value with peaches, pears, prunes in sirup, and Royal Anne cherries.

PEACHES (FIGURE 4). Correlations are shown for three different years. Thirty-seven different lots of plate representing steel-manufacturing and steel-composition variables were packed in 1932. Thirty-seven different lots of tin plate were packed in 1933, and seven different lots were packed in 1934. Each lot consisted of 50 to 100 cans representing the same number of sheets of tin plate.

The curves represent the average hydrogen evolution value of each lot plotted against the average can service value.

Low hydrogen evolution values are associated with low can service value and as the hydrogen evolution value increases, the can service value increases. In general, the slope of the curve changes in the range 27 to 35 hours on the ordinate. Below this range, a small increase in hydrogen evolution value is associated



with a large increment in can service value. Above this range, the relation is reversed. The identical correlation was not found each year, however. The 1933 peaches were evidently more corrosive than those of 1932 and 1934. That the fruit variable is responsible for the lower can service value of the 1933 pack is borne out by the curves. Two packs were made this year. The

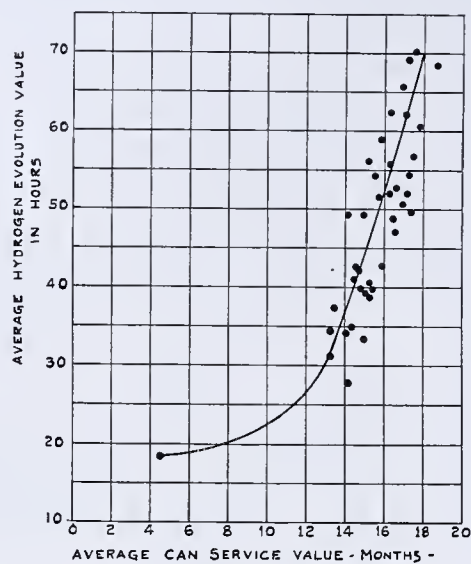


FIGURE 5. CORRELATION OF CAN SERVICE AND HYDROGEN EVOLUTION VALUES FOR PEARS

1933 B pack (with different lots of tin plate than used in the 1933 A pack) was made later in the season than the 1933 A pack and has considerably higher can service value for a comparable hydrogen evolution value. The reason for this difference has not been determined.

**PEARS (FIGURE 5).** This curve shows the correlation found with pears packed in 1933 in 40 different lots of plate. Here again low hydrogen value is associated with low can service value and a break in the curve is noted at about 25 hours on the hydrogen evolution scale.

**PRUNES (FIGURE 6).** A similar relationship exists for dried prunes in sirup. Packs were made in 1933 (40 lots) and in 1934 (7 lots). This product is one of the most corrosive packed in plain cans and the curves show more scatter than was found with the other fruits tested. Of interest is the 1934 pack correlation which has one point (marked with an arrow) that has much shorter service life than would be expected from its hydrogen evolution value. This point represents one lot of tin plate having an appreciable copper content in the steel base (0.15 per cent).

Figure 7 was drawn to illustrate the relationship between the rate of hydrogen springer formation and the distribution of the hydrogen evolution values obtained on the same lots of tin plate. These curves were constructed from the data of the 1934 pack of prunes in sirup. Each code represents an individual lot of plate.

The solid lines show the per cent of hydrogen springers plotted against time in days, while the dotted lines show the per cent of hydrogen evolution 5-cc. failures (time to produce 5 cc.) plotted against time in hours. It is interesting to note the identical nature of the curves for lots R and SE.

**ROYAL ANNE CHERRIES (FIGURE 8).** Royal Anne cherries were packed in 1934 in seven lots of tin plate. The correlation is very good and is similar to that found with peaches and pears. One lot (marked with an arrow) falls off the curve. This is a copper-bearing steel-base tin plate, the same one mentioned under prunes.

### Limitations of the Hydrogen Evolution Test

As is true with all accelerated corrosion tests, individual values show considerable variation and it is impossible to predict service value on the basis of individual tests. In spite of the individual variations, fairly accurate predictions of the service value of different lots of plate known to be produced of uniform steel are possible, provided correlating data have shown that variations in alloy content of the steel, such as the presence of copper, do not have a specific effect on service life with the specific fruit tested.

As pointed out previously, the corrosiveness of a certain type of fruit varies from year to year and results in a shifting of the correlation curve along the storage time axis. In spite of the fruit variable, low hydrogen evolution values are always associated with low can service values.

Copper in the steel, above 0.10 per cent, results in shorter service life of plain cans packed with Royal Anne cherries and with dried prunes in sirup, but does not substantially affect the service life of plain cans packed with peaches or pears nor does it affect the hydrogen evolution values. This effect of copper is more significant with enameled can packs

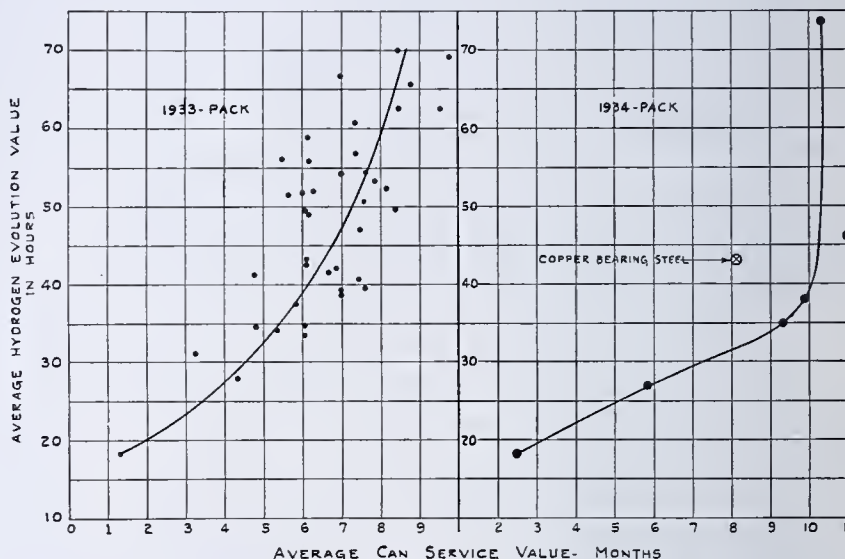


FIGURE 6. CORRELATION OF CAN SERVICE AND HYDROGEN EVOLUTION VALUES FOR PRUNES

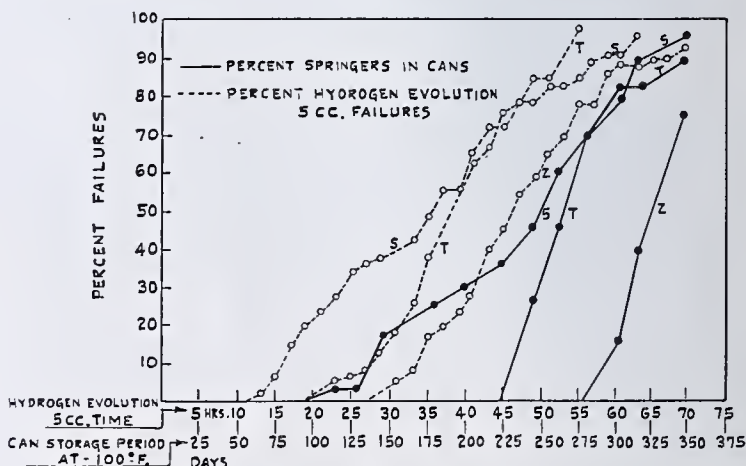
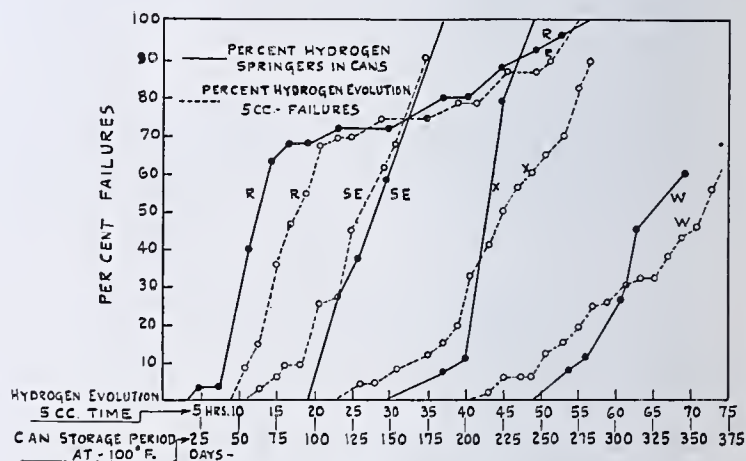


FIGURE 7. RELATIONSHIP BETWEEN RATE OF HYDROGEN SPRINGER FORMATION AND DISTRIBUTION OF HYDROGEN EVOLUTION VALUES

Prunes in sirup



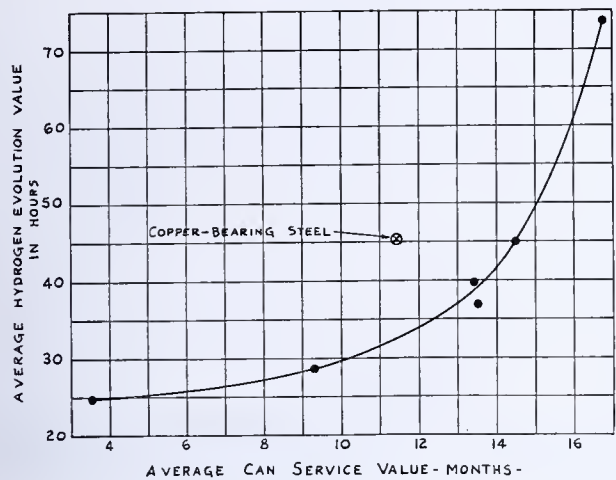


FIGURE 8. CORRELATION OF CAN SERVICE AND HYDROGEN EVOLUTION VALUE FOR CHERRIES

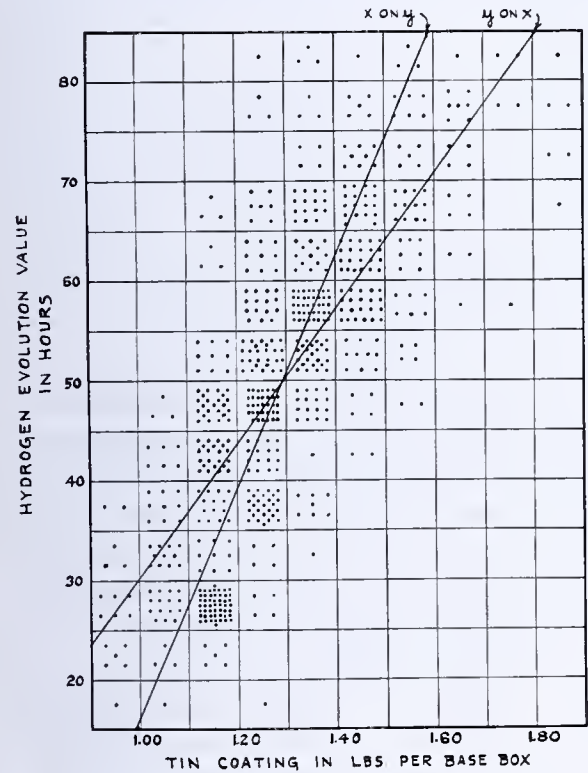


FIGURE 9. HYDROGEN EVOLUTION VALUE vs. TIN COATING WEIGHT  
Hot-pack rolled plate

of red sour pitted cherries and black cherries, which show about four times longer service life with cans made of low metalloid strip steel (type L) having less than 0.04 per cent of copper than is found with cans of the same steel having 0.18 per cent of copper. These data contradict the conclusions of Hoar and Havenhand (5), who contend that the copper content of steel for tin plate should be at least twice its sulfur content. As with the hydrogen evolution test, this amount of copper (0.18 per cent) does not affect the service life of enameled cans packed with loganberries. This specific effect of copper has been checked in this laboratory with a number of controlled experimental packs.

**Correlation of Hydrogen Evolution Value with Tin Coating**

The variation in test values on a given lot of plate is due partially to variation in the continuity and thickness of the tin coating and to other surface conditions. It is usually agreed that increased tin coating weight results in an in-

creased corrosion resistance. This is generally true of the hydrogen evolution test, but the correlation between tin coating weight and hydrogen evolution value is not perfect. Other factors besides weight of tin coating (as measured by the Sellars method, 12) contribute to the hydrogen evolution value. Surface condition and steel base composition have a very significant bearing on corrosion rate. This will be the subject of a future paper.

Figures 9 and 10 show scatter diagrams and regression curves of the tin coating weight-hydrogen evolution value relationship on cold-rolled strip (type L) and hot-pack rolled plate. The tin coating weight was determined on a ring 25.8 sq. cm. (4 square inches) in area concentric to the test specimen and includes the tin on both sides of the specimen. Each dot represents an individual determination. Hydrogen evolution values are grouped in 4-hour intervals and the tin coating weights are grouped in 0.10 pound (2.242 grams per square meter) per base box intervals.

In Figures 9 and 10, lines showing the regression of  $x$  on  $y$  are given, as well as the more usual regression of  $y$  on  $x$ . The first is used to estimate the most probable value of  $x$  for a given value of  $y$ . The second, showing the regression of  $y$  on  $x$ , is used to estimate the most probable value of  $y$  for a given value of  $x$ .

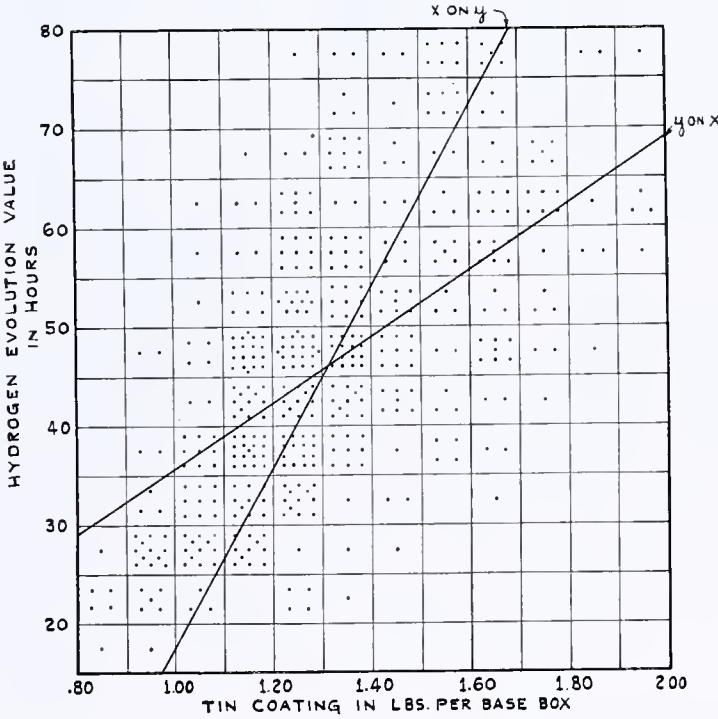


FIGURE 10. HYDROGEN EVOLUTION VALUE vs. TIN COATING WEIGHT  
Cold-rolled strip plate

**Summary**

A simple test for the corrosion resistance of tin plate based on the rate of hydrogen formation resulting from the attack of  $N$  hydrochloric acid on a standard tin plate specimen is described.

Correlations between hydrogen evolution values and can service values of plain cans packed with peaches, pears, Royal Anne cherries, and prunes in sirup indicate that the test gives reasonably accurate predictions of can service value.

Certain metallic alloying constituents of the steel base affect the can service value with some foods, but do not show a corresponding effect on the hydrogen evolution value. Copper lowers the can service value of Royal Anne cherries and



prunes in sirup, but has no effect on the service value of peaches or pears.

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# Relation between Volatile Matter and Hydrogen-Carbon Ratio of Coal and Its Banded Constituents

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Using data from the literature and paying special attention to the petrography, the relation between volatile matter and hydrogen-carbon ratio was studied. Plotting these two values against each other gave two curves, approximated by three straight lines. Anthraxylons (vitrain and clarain) are found on one curve, whereas the other constituents (fusains, attrital matter, durains, and spores) occur on the other. The equations representing these straight lines can be used to relate the volatile matter and hydrogen-carbon ratios of the constituents with moderate accuracy.

A more interesting and useful relationship is that between the volatile matter and the square of one hundred times the hydrogen-carbon ratio. Two straight lines result when these are plotted. Vitrains and clarains fall on the shorter line, and

the other constituents fall on the longer line.

Equations defining these lines apply with fair accuracy to anthraxylons of all ranks and to other constituents from low-volatile fusains to high-volatile spores. Probably most important is the determination of the approximate petrographic composition of coals from proximate and ultimate analyses, but the equations should be useful also in ascertaining the quality of isolated constituents and in correlating chemical reactions of coal with its rank and petrography.

By plotting volatile matter against the sum of the hydrogen and carbon contents and using these equations, a satisfactory estimate of the petrography can be made in many instances from the proximate and ultimate analyses.

SEVERAL investigators have noted relationships between the volatile matter and the carbon and hydrogen contents of various coals. Ralston (12) constructed a chart that gives the carbon, hydrogen, and oxygen contents and volatile matter content of carbonaceous materials ranging from anthracites to wood and plants. Korn (9) and Schuster (14) claim that a linear relationship exists between carbon content and volatile matter, a conclusion that has been disputed by Seyler (15). In studying the connection between proximate and ultimate analyses, Pallot (11) plotted carbon, hydrogen, and oxygen contents against fixed carbon. Spooner (16) proposed several equations that relate volatile matter and ultimate analyses of coals. Although these relationships may be useful and fairly satisfactory, no distinction was made between the type and proportion of petrographic constituents present.

More recently, Seyler (13, 15) pointed out that the petrographic composition of the coal exerts an important influence on the relation between volatile matter and carbon and hy-

drogen contents. Bright coals (chiefly anthraxylon or vitrain and clarain) were characterized by the following formula, where, as later in this paper,  $V$ ,  $C$ , and  $H$  represent percentages of volatile matter, carbon, and hydrogen, respectively.

$$V = 10.61H - 1.24C + 84.15$$

It was claimed that coals not conforming to this equation (dry, mineral-matter-free basis) contain considerable amounts of banded constituents other than vitrain or clarain and that, therefore, some information as to the petrography of the coal can be obtained from the proximate and ultimate analyses. Other equations relating volatile matter of bright coals with carbon or hydrogen content are:

$$\text{Seyler's (15) logarithmic: } H = 2.80 \log V + 0.95$$

$$\text{Diederichs' (2): } H = V \left( \frac{7.35}{V + 10} \right) - 0.013$$

$$\text{Seyler's (15) quadratic: } \begin{aligned} H &= 0.1292V - 0.00156V^2 + 2.69 \\ C &= 0.299V - 0.01334V^2 + 90.79 \end{aligned}$$



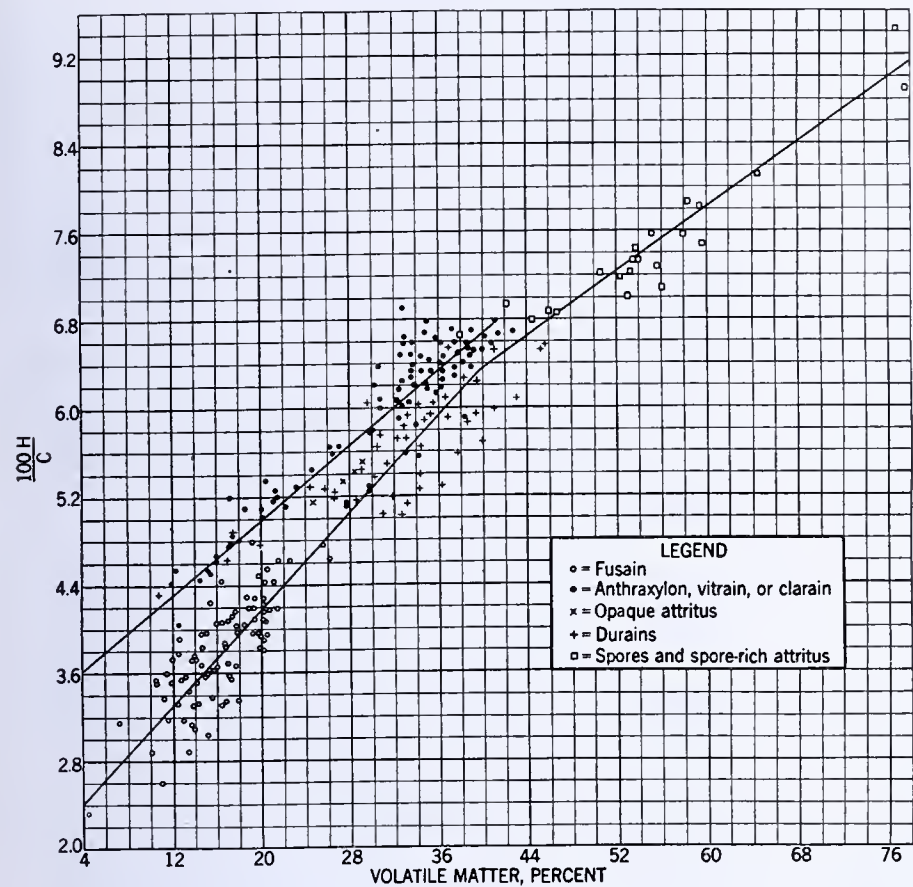


FIGURE 1. RELATION BETWEEN VOLATILE MATTER AND HYDROGEN-CARBON RATIO

In the present work it was found that a definite relationship exists between the hydrogen-carbon ratio and volatile matter of anthraxylon (vitrain), attrital matter, durain, fusain, and spores (dry, ash-free basis). Plotting the hydrogen-carbon ratio against the volatile matter gives two curves; vitrains and clarains fall on one curve, and fusains, durains, and spores on the other. These two curves can be approximated fairly well by three straight lines (Figure 1). The equations representing these lines can be used to relate the volatile matter and hydrogen-carbon ratios of the macroconstituents with moderate accuracy. For example, vitrains and clarains are characterized by the equation

$$V = \frac{1185H}{C} - 39.2 \tag{1}$$

Fusains and durains containing volatile matter up to about 41 per cent conform to the equation

$$V = \frac{923H}{C} - 18.5 \tag{2}$$

For spores, spore-rich attritus, and durains of more than 41 per cent volatile matter the following equation can be used:

$$V = \frac{1365H}{C} - 46.9 \tag{3}$$

A more interesting and useful relationship is that between the volatile matter and  $\left(\frac{100H}{C}\right)^2$ . Two straight lines are obtained when the

volatile matter and  $\left(\frac{100H}{C}\right)^2$  of coal constituents are plotted (Figure 2). Vitrains and clarains fall on the upper line, which is defined by the equation

$$V = \frac{13}{12}\left(\frac{100H}{C}\right)^2 - 7.6 \tag{4}$$

Vitrains falling on the upper end of the vitrain-clarain line (above about 43 per cent volatile matter) were not found, and analytical data for vitrains of extremely high or low rank were not included in Figures 1 and 2. The other constituents fall on the lower line and are represented by Equation 5.

$$V = \frac{17}{18}\left(\frac{100H}{C}\right)^2 + 2.3 \tag{5}$$

$$V = \left(\frac{100H}{C}\right)^2 \tag{6}$$

Equation 6 is simpler and gives results almost as accurate as those obtained with Equation 5 (Tables II to IV).

The agreement between the volatile matter and the values calculated by these formulas is shown by Tables I to IV, which, in some instances, give also the volatile matter calculated by Seyler's equation ( $V = 10.61H - 1.24C + 84.15$ ). Unusually accurate calculations are shown for the vitrains in Table I, possibly because these samples were carefully selected by Seyler (15) and the analytical data were calculated to the dry, mineral-matter-free basis.

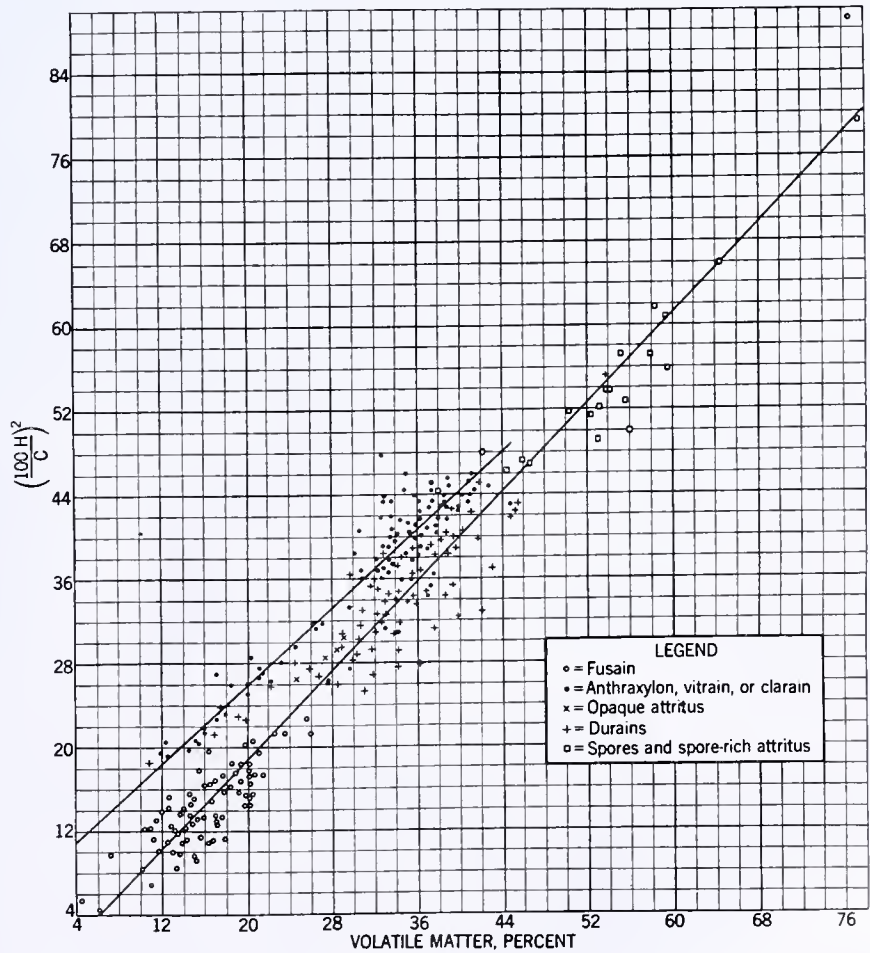


FIGURE 2. RELATION BETWEEN VOLATILE MATTER AND  $\left(\frac{100H}{C}\right)^2$



TABLE I. VITRAINS (SEYLER)

Carbon %	Hydrogen %	Volatile Matter		
		Determined %	Seyler's formula %	Calculated from Equation 4 %
86.35	5.32	32.62	33.53	33.5
91.39	4.65	18.45	20.17	20.6
89.46	5.05	26.24	26.80	26.9
89.50	4.86	24.61	24.73	24.3
91.74	4.42	17.47	17.29	17.6
88.42	5.30	30.75	30.74	31.3
92.39	4.03	12.47	12.34	13.0
91.13	4.69	21.11	20.91	21.1
91.62	4.37	17.33	16.91	17.0
80.90	5.39	41.43	41.03	40.5
91.35	4.74	21.48	21.17	21.6
91.90	4.28	16.04	15.61	15.9
92.01	4.37	17.23	16.42	16.8
85.92	5.46	36.29	35.54	36.3
90.91	4.80	23.20	22.35	22.6
87.83	5.07	29.85	29.03	28.5
91.38	4.57	20.09	19.33	19.5
91.81	4.41	18.04	17.10	17.4
86.92	5.32	33.70	32.83	33.0
91.93	4.24	16.03	15.15	15.4
92.25	4.18	15.23	14.11	14.6
88.46	5.11	29.76	28.68	28.6
88.17	5.09	30.02	28.82	28.6
90.55	4.63	22.26	20.99	20.7
86.96	4.90	27.10	28.31	26.8
85.03	5.41	37.52	36.11	36.2
92.30	4.10	14.53	13.20	13.8
83.45	5.44	39.95	38.39	38.4
92.42	4.16	15.45	13.69	14.4

The data of Wandless and Macrae (20) were used in making the calculations in Table II, which compares the determined and calculated values for volatile matter of fusains and gray durains. The agreement of determined and calculated values for spores and spore-rich and opaque attritus is shown in Table IV. If a few gray durains and spores are excluded, the agreement is good in most instances. Equations 5 and 6 appear to apply with fair accuracy over the entire range of coal constituents (excluding vitrains and clarains) from the low-volatile fusains to the high-volatile spores.

Since there is not necessarily a definite relation between the hydrogen-carbon ratio and the sum of the hydrogen and carbon contents, the latter values ( $C + H$ ) were plotted against the volatile matter of the banded constituents of coal. The resulting figure (Figure 3) also shows promise of being useful in predicting petrographic composition and evaluating the purity of coal macro-constituents. Only the low-volatile (high content of opaque matter) and high-volatile (spore-rich) durains are shown in Figure 3; durains of intermediate volatile matter fall in Figure 3 somewhere between the spores and the opaque attritus, presumably according to rank and their content of these two substances. As might be expected, the coal hydrogenation residues (Table VI) fall rather well on the lower half of the fusain line (extreme left of Figure 3). However, as judged by Equations 4 and 5, these residues contain considerable amounts of material other than fusinite (15).

### Applications

An obvious and relatively unimportant benefit to be derived from Figure 2 and Equations 3 and 4 is the calculation of volatile matter from the ultimate analysis. Conversely, the hydrogen-carbon ratio can be calculated from the volatile matter and, by some features of methods previously employed (2, 14, 15), the percentages of carbon and hydrogen can be estimated.

The formulas and figures of the present paper were constructed in an attempt to facilitate the correlation of hydrogenation data (3, 5, 7) with both the petrography and rank of coal. It is likely that the relationships outlined herein will be helpful in several respects. By applying Equations 4 and 5 (or Seyler's vitrain formula, 15) some clue as to the petrographic composition of coals is afforded by the proximate and ultimate analyses, even when the coal petrographer's analysis is lacking. Further, a method of checking the quality of banded constituents isolated from coal is offered.

TABLE II. FUSAINS AND GRAY DURAINS

Carbon %	Hydrogen %	Volatile Matter		
		Determined %	From Equation 6 %	From Equation 5 %
Fusains				
90.4	3.2	12.8	12.5	14.1
91.6	2.9	13.8	10.0	11.8
89.2	3.4	19.8	14.6	16.0
90.5	3.1	13.5	11.7	13.4
90.9	3.0	13.9	10.9	12.6
89.2	3.8	20.2	18.2	19.4
88.3	3.5	17.8	15.7	17.1
89.6	3.2	17.1	12.7	14.3
93.9	2.7	10.1	8.3	10.1
91.0	3.2	14.2	12.4	14.0
91.2	3.6	14.6	15.6	17.0
Gray Durains				
86.2	4.8	31.5	31.0	31.6
83.4	4.6	30.7	30.4	31.0
84.9	5.0	34.9	34.7	35.1
83.4	4.7	29.3	31.8	32.3
87.8	4.9	33.0	31.1	31.7
86.5	4.9	32.0	32.1	32.6
84.8	4.9	34.0	33.4	33.9
85.3	4.7	32.4	30.4	31.0
86.1	5.0	34.9	33.7	34.2

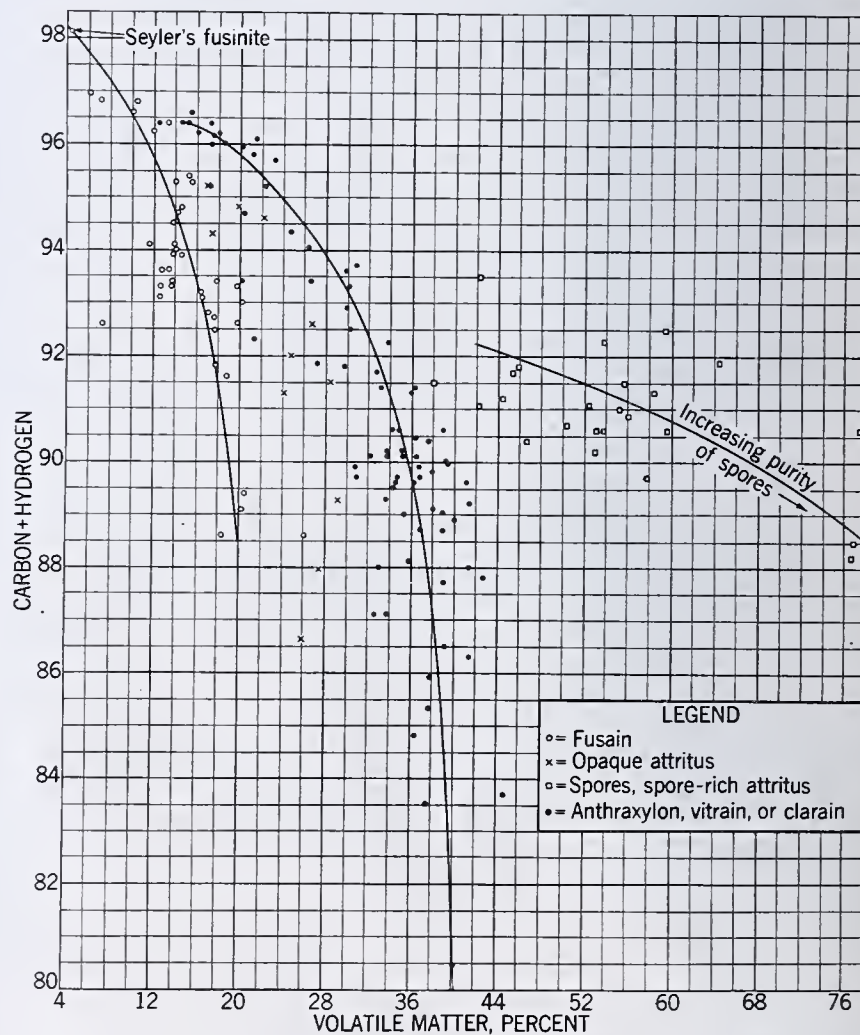


FIGURE 3 RELATION BETWEEN VOLATILE MATTER AND CARBON PLUS HYDROGEN



TABLE III. GRAY DURAINS (SEYLER)

Carbon %	Hydrogen %	Volatile Matter	
		Determined %	From Equation 5 %
90.52	4.32	19.87	23.7
88.47	4.94	30.70	31.7
86.59	4.95	32.33	33.2
86.83	5.43	38.17	39.2
82.94	4.17	30.96	26.1
88.80	5.01	32.68	32.4
86.52	5.39	39.63	39.0
81.93	4.31	34.24	28.4
84.45	4.56	34.20	29.8
84.40	5.02	39.40	35.7
82.00	4.98	43.08	37.1
86.07	5.61	45.31	42.5

TABLE IV. SPORES AND SPORE-RICH AND OPAQUE ATTRITUS

	Refer- ence	Carbon %	Hydrogen %	——Volatile Matter——		
				Deter- mined %	From Equa- tion 6 %	From Equa- tion 5 %
Opaque attritus	18	87.5	4.5	24.7	26.4	27.3
	18	86.8	4.7	28.4	29.3	30.0
	8	84.6	4.65	29.09	30.2	30.8
	8	83.5	4.45	27.4	28.4	29.1
Spore-rich attritus	18	85.8	5.7	38.0	44.1	44.0
	18	85.2	5.9	42.1	47.9	47.5
	18	85.4	5.8	44.4	46.1	45.8
	1	84.64	6.65	58.3	61.7	60.5
	1	84.42	6.2	53.8	53.9	53.2
	1	84.64	6.1	50.3	52.0	51.4
	1	84.6	5.8	46.6	47.0	46.7
Spores	17	80.6	7.6	76.6	88.9	86.3
	10	85.0	6.9	64.4	65.9	64.6
	19	83.2	7.4	77.5	79.1	77.0
	17	80.9	7.6	76.8	88.2	85.6

From the results thus far available in the literature, it appears that the amenability of constituents to hydrogenation can be judged by their location on Figure 1 or 2. The fusains (7, lower end of fusain-durain-spore line) give low hydrogenation yields, whereas spores (3, 5, upper end of same line) are easily hydrogenated. Although less resistant than fusains, durains containing opaque matter are difficult to hydrogenate (5). Anthraxylons, occurring on the upper line in Figure 1 or 2, generally give high liquefaction yields (5, 7).

To obtain a more complete picture of the hydrogenation of coal constituents, the components of the banded constituents also should be considered. For example, the liquefaction of fusain by hydrogenation probably is limited by the fusinite (inerts) present. The vitrain-like material (vitrinite) in fusain is amenable to hydrogenation. Similarly, the liquefaction of anthraxylon appears to be limited by the presence of small amounts of inert material (possibly that determined by Francis' rational analysis, 4, 5, or similar oxidation methods). It has been observed in several instances that hydrogenation and oxidation yield about the same amount of inert matter (6, 21).

An example of the use of Figure 2 in predicting liquefaction yields is afforded by the first vitrain listed in Table V. Although described (7) as vitrain, it occurs in Figure 2 far below the vitrain line. On hydrogenation (7) there was obtained a 48.8 per cent yield of inert material with a composition considerably different from the original sample. Therefore, the vitrain was of poor quality and lacking in homogeneity unless the inert residue was produced during the hydrogenation. Since the residue has a carbon-hydrogen ratio higher and volatile matter lower than the original vitrain, it is likely that, if produced during the hydrogenation, carbonization was responsible for its presence. The two clarains, which are defined better by Equation 4 than by Equation 5 (indicating the presence of much anthraxylon), were hydrogenated satisfactorily (7). Comparison of the determined volatile matter of the fusain in Table V with the volatile matter calculated by Equations 4 and 5 indicates that only negligible amounts of

vitrinite are present. This was confirmed by the hydrogenation experiment, since only a negligible amount was liquefied (7).

Although it has been assumed (21) that coal hydrogenation residues are virtually pure fusain, petrographic analyses of the inert residues usually are not available. However, proximate and ultimate analyses have been published (7), and some clue as to the petrographic composition of the residues can be derived from these analyses by means of Equations 4 and 5. Table VI contains such data on residues obtained by Graham and Skinner (7) on hydrogenating various coals. From Table VI it is evident that the inert residues resemble low-volatile durains or opaque attritus rather than vitrains. This agrees with Francis' claim (5) that reactive clarains are suitable for hydrogenation whereas the opaque matter in durains is not.

TABLE V. COMPOSITION OF BANDED CONSTITUENTS AND THEIR INERT RESIDUES

(Dry, ash-free basis. Reference 7)							
Num- ber	Constituent	Carbon %	Hydro- gen %	Volatile Matter		C/H Ratio	
				Deter- mined %	From Equa- tion 4 %	From Equa- tion 5 %	
1	Vitrain	79.83	5.74	41.1	48.4	51.1	13.9
	Residue (48.8%)	85.91	4.24	15.2	18.8	25.3	20.3
2	Clarain	81.25	5.27	39.1	38.0	42.1	15.4
	Residue (21.8%)	89.23	3.76	..	..	..	23.7
3	Clarain	84.19	5.47	35.4	38.1	42.2	15.4
	Residue (16.4%)	85.86	3.93	19.2	15.1	22.1	21.9
4	Durain	82.44	5.08	34.5	33.5	38.2	16.2
	Residue (37.5%)	89.74	3.97	..	..	..	22.6
5	Fusain	94.96	1.99	6.1	-2.8	6.4	47.7
	Residue (ca. 95%)	..	..	..	..	..	..

TABLE VI. COMPOSITION OF INERT RESIDUES  
(Dry, ash-free basis)

Carbon %	Hydrogen %	Volatile Matter		
		Determined %	From Equation 4 %	From Equation 5 %
87.74	3.88	19.1	13.6	20.8
90.89	3.70	14.4	10.3	17.9
90.98	4.08	17.3	14.2	21.3
89.89	3.88	18.6	12.6	19.9
90.01	3.90	21.7	12.7	20.0
90.69	3.63	14.6	9.8	17.4
92.47	3.60	13.7	8.8	16.6
92.93	3.54	10.2	8.1	16.0
89.80	3.70	14.0	10.8	18.3

It should not be necessary to point out that uncertainties in determining accurately the volatile matter and carbon and hydrogen contents of coal on the dry, mineral-matter-free basis make correlation of these properties difficult. It is likely that the relation between volatile matter and ultimate analysis can be determined much more precisely when reliable data, calculated to the dry, mineral-matter-free basis, are available.

### Acknowledgment

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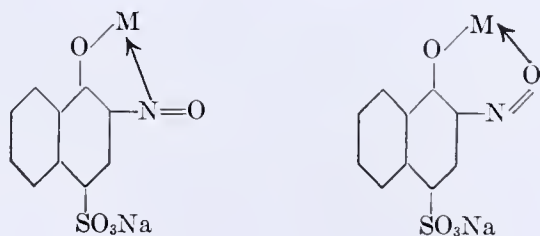
## Detection of Cobalt, Copper, and Ferrous Iron With 2-Nitroso-1-Naphthol-4-Sulfonic Acid

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IMMEDIATELY after the description by Ilinski (2) of the reaction which takes place between cobalt and 1-nitroso-2-naphthol, Hoffmann (1) called attention to the fact that he had observed it in 1883, when he prepared and studied not only this compound, but also 2-nitroso-1-naphthol and 2-nitroso-1-naphthol-4-sulfonic acid. The latter substance is a dyestuff, and its preparation was patented in 1884, with the claim that it gave a green with iron and a red with cobalt.

The free acid is a brownish yellow crystalline substance, very stable, and easily soluble in water. It is strongly acidic, and capable of forming two series of salts; however, only the hydroxyl group is involved in its most characteristic color reactions, the hydrogen being replaced by one equivalent of the metal, which then forms a coördinate bond with either the nitrogen or the oxygen of the neighboring nitroso group to give a five- or six-membered chelate ring:



Since the strains, and therefore the stabilities, of five- and six-membered rings are so nearly equal, it is difficult to say which of the two structures is correct.

The reagent may be prepared easily, and with excellent yields, by the action of nitrous acid upon 1-naphthol-4-sulfonic acid, according to the method of Witt and Kaufmann (3). A 1 per cent solution is made up in water, and is stable for several months, at least.

Although it forms sparingly soluble salts with several metals, none is sufficiently insoluble to make it of value as a precipitant. However, it gives beautiful red, orange, and green color reactions with cobalt, copper, and ferrous iron, respectively. In concentrated solutions precipitates are formed, but from dilute solutions the dyestuffs do not settle out, and are stable over a period of months.

The reaction with ferrous iron is most intense at a pH of 5, and the colors are markedly weaker at higher and lower acidities. With cobalt, on the other hand, a greater latitude is permissible, and the most favorable range is 7 to 8; however, if the solutions are not too dilute, good colorations can be obtained at any pH greater than 3. Ferric iron gives a much weaker color reaction than do cobalt, copper, and ferrous iron, but nevertheless enough to cause interference; this can be suppressed by the addition of fluoride. No means have been found for suppressing the mutual interference of the other ions, but ferrous iron can be oxidized to ferric, which does not interfere in the presence of fluoride. Copper can be removed as sulfide, and cobalt may be removed by classical methods when required. However, they may usually be recognized in the presence of each other by the color. Nickel interferes only when present in high concentration; it is possible to detect cobalt in the presence of 1000 times as much nickel, or more. Chromium and other common ions, except cyanide, do not interfere; cyanide prevents the reaction from taking place.

The sensitivity of the test is very great. When none of the interfering ions is present, it is comparatively easy to detect cobalt or iron in concentrations of one part in 20 million; the colors given by copper are only slightly less intense. Blanks must be used for the great dilutions, since the reagent itself is yellow. It is also necessary to allow some time for the color to develop in very weak solutions; the reaction may be speeded up by heating. About 0.01 gamma can be detected by means of a spot test for either of the three metals; when a sufficient sample is available, it is convenient to work in Nessler cylinders, adjusting the pH with sodium acetate and acetic acid.

The study of these reactions is being continued, with the object of adapting them to quantitative colorimetric determinations.

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# An Improved Kurt Meyer Titration

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MEYER (1) proposed the direct titration of the enolic form of a tautomeric compound with an alcoholic bromine solution, and also an indirect bromine titration method. In the indirect method the compound was dissolved in 96 per cent alcohol and cooled to 10° C., and an excess of an alcoholic bromine solution was added. This excess was removed by adding a small amount of sodium thiosulfate solution. Then a potassium iodide solution was added, and the liberated iodine was titrated with a solution of sodium thiosulfate. Later Meyer and Kappelmeier (2) proposed the use of 2-naphthol, in place of sodium thiosulfate, to absorb the excess bromine.

The authors have had some experience with this indirect titration method and have attempted to improve upon its accuracy. 2-Naphthol and its alcoholic solutions are usually colored brown, even after the compound has been carefully purified. This makes it difficult, in many cases, to ascertain the point at which all the excess bromine has been removed, and also causes an error when the alcoholic solution containing free iodine is titrated with sodium thiosulfate until the yellow color due to iodine has been removed. This condition can be remedied by using a compound such as diisobutylene which will absorb bromine by forming a colorless bromide, but will not react with iodine to form a stable compound.

The purpose of this investigation was to ascertain if diisobutylene could be used in place of 2-naphthol in the indirect Kurt Meyer titration.

## Preparation of Reagents

The dibenzoylmethane was prepared according to the method given by Pond, York, and Moore (3), and was further purified by repeated recrystallizations from methyl alcohol, yielding a practically colorless substance.

The iodine was sublimed twice. An approximately 0.1 *N* solution of sodium thiosulfate was prepared and allowed to stand for several months, protected from the atmosphere by a tube filled with soda lime. The diisobutylene was the practical grade obtained from the Eastman Kodak Company. All the other reagents were c. p. products.

## Titrations

A sample of dibenzoylmethane was weighed, placed in a wide-necked Erlenmeyer flask, and dissolved in 25 ml. of absolute

methyl alcohol. The resulting solution was cooled to -5° C. and an excess of an approximately 0.1 *N* solution of bromine in absolute methyl alcohol was added. The solution was mixed well, and a slight excess of diisobutylene was added. The time consumed in adding the bromine and absorbing the excess of it was about 15 seconds. Then 5 ml. of a 10 per cent aqueous solution of potassium iodide were added and the mixture was warmed to 30° C. by dipping the flask in hot water while swirling its contents around. The solution was allowed to stand 5 to 10 minutes and was titrated with an approximately 0.1 *N* solution of sodium thiosulfate until the color had become a light yellow. Then 250 ml. of water and 4 ml. of a 0.6 per cent potato starch solution, which had been filtered, were added and the titration was continued to the disappearance of the blue color. Some titrations were made without using water and starch.

These titrations were compared with others which were performed according to the indirect Kurt Meyer method, with the exception that after the potassium iodide solution had been added the titration was carried out as above. The results of these and the first titrations are given in Table I.

The sodium thiosulfate solution was standardized according to the method of Treadwell and Hall (4) using iodine as the primary standard. The mean of these titrations was 0.1003 *N*, and the average deviation 1 part per 1000.

## Discussion

Solutions of bromine in ethyl alcohol are not very stable, but a solution in methyl alcohol retains its strength for a longer time. Therefore absolute methyl alcohol was employed in preparing all the alcoholic solutions used.

The proposed method gives better agreement of results than the original indirect Kurt Meyer method. Some experiments, not included in the table, which were performed by using the indirect Kurt Meyer method, gave variations of the same magnitude. The end point in the authors' titration is sharper and a blue color is always produced with starch, while gray-blue colors are often obtained when Kurt Meyer titrations which employ 2-naphthol are performed under the same conditions. The amount of precipitate formed upon dilution in the original Kurt Meyer titration is greater than that formed when the proposed method is employed. The authors have found it possible to titrate the liberated iodine without dilution and addition of starch if their procedure is used. The end point is sharp and the brown color due to excess 2-naphthol is not present to cause an error in the results. The excess of diisobutylene does not form a precipitate, but floats on the surface as an oil and gradually evaporates.

The mean of the authors' titrations is 95.66 per cent. This represents the approximate percentage of enol under the conditions of the experiment.

The authors believe that they have improved the Kurt Meyer titration because their titrations agree within 1 per cent, while the indirect Kurt Meyer titration gives variations as high as 7 per cent.

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TABLE I. TITRATION OF DIBENZOYLMETHANE WITH SODIUM THIOSULFATE SOLUTION

$C_{15}H_{12}O_2$ Gram	0.1 <i>N</i> Bromine Solution Ml.	Thiosulfate Solution Ml.	Decolorizing Agent	Enol $C_{15}H_{12}O_2$ %
0.2421	25	20.65	$C_8H_{16}$	95.88
0.2407	25	20.45	$C_8H_{16}$	95.52
0.2114	25	18.00	$C_8H_{16}$	95.79
0.2651	25	22.45	$C_8H_{16}$	95.25
0.1799	25	15.40	$C_8H_{16}$	96.15
0.3489	40	29.50	$C_8H_{16}$	95.16
0.2665	35	22.70	$C_8H_{16}$	95.70
0.4505	52	38.50	$C_8H_{16}$	96.07
0.2795	30	23.72	$C_8H_{16}$	95.43
0.2257	25	19.30	$C_8H_{16}$	96.07
0.2774	30	23.52	$C_8H_{16}$	95.34
0.2035	25	17.35	$C_8H_{16}$	95.88
0.1964	25	16.70	$C_8H_{16}$	95.70
0.2206	25	18.75	$C_8H_{16}$	95.52
0.2076	25	17.62	$C_8H_{16}$	95.43
0.1991	25	16.95	$C_8H_{16}$	95.70
0.2382	30	19.90	$C_{10}H_7OH$	93.74
0.2551	30	20.60	$C_{10}H_7OH$	90.85
0.2403	35	19.85	$C_{10}H_7OH$	92.86
0.2486	30	21.00	$C_{10}H_7OH$	94.97
0.2128	30	18.00	$C_{10}H_7OH$	95.07
0.1797	30	15.75	$C_{10}H_7OH$	98.52



# Systematic Scheme of Identification

TABLE I. IDENTIFICATION

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 Ephedrine	+	—	—	—	—	R	—	—	—	—	—	—	dk br Y	—
2 Cocaine	—	+	Y ppt	—	—	—	—	—	—	—	—	—	—	—
3 Procaine	—	—	W ppt	—	—	R	—	—	—	—	—	—	—	—
4 Colchicine	—	—	—	Or	—	dk G	—	Y	y Br	—	—	—	lt br Y	G
5 Cotarnine	—	—	—	—	G	dk R	—	—	br R	—	—	—	lt br Y	Or R
6 Theobromine	—	—	—	—	B	—	—	—	—	—	—	—	—	—
7 Arecoline	—	—	—	—	—	ΔG	—	—	—	—	—	—	—	—
8 Caffeine	—	—	—	—	—	—	B	—	—	—	—	—	—	—
9 Nicotine	—	—	—	—	—	—	—	Pk	Ro	—	—	—	—	—
10 Piperine	—	—	—	—	—	br R	—	YΔG	Br	—	—	—	y BrΔbr R	Or R
11 Veratrine	—	—	—	—	—	—	—	—Pk	Y	L	—	—	—	Or R
12 Quinidine	—	—	—	—	—	—	—	B fl	—	—	—	—	YΔ—	—
13 Quinine	—	—	—	—	—	—	—	B fl	Y	—	—	—	YΔ—	—
14 Heroine	—	—	—	—	—	r Br	—	—	V	—	—	—	lt Y	Y
15 Hyoscyamine	—	—	—	—	—	—	—	—	Y	—	—	—	lt Or YΔOr Y	—
16 Atropine	—	—	—	—	—	—	—	—	—	L	—	—	—	—
17 Hashish	—	—	—	—	—	—	—	—	—	—	P	—	—	—
18 Codeine	—	—	Y ppt	—	—	dk G	—	—	PkΔV	—	—	L	lt Or Y	Y
19 Apomorphine	—	—	—	—	—	dk G	—	—	dk R	Or R	Cr	—	ol GΔbr Y	RΔOr Br
											layer over insol. sol.			
20 Yohimbine	—	—	—	—	—	PΔdk G	—	—	—	—	—	—	lt YΔbl V	PΔol G
21 Berberine	—	—	—	—	—	dtty G	—	Y	br R	—	—	—	—	dk R
22 Strychnine	—	—	—	—	—	P	—	—	—	—	—	—	Or RΔY	VΔOr R
23 Brucine	—	—	—	—	—	R	—	—	—	—	—	—	Y	Or
24 Physostigmine	—	—	Y ppt	—	—	—	—	—	y Br	—	Cr	—	—	Or RΔBr
25 Pilocarpine	—	—	Y ppt	—	—	Or R	—	—	—	—	—	—	—	—
26 Dilaudid	—	—	—	—	—	P	ol G	—	Ro	—	—	—	lt Or YΔ—	—
27 Hydrastine	—	—	—	—	—	br R	—	—	br R	—	—	—	Or RΔbr Y	y Br
28 Papaverine	—	—	—	—	—	dtty G	—	—	V	—	—	—	br R	Or R
29 Thebaine	—	—	—	—	—	dk br R	—	Y	Br	—	—	—	Or R	Or
30 Morphine	—	—	—	—	—	br G	G	—	V	—	—	—	—	Y-30
31 Dionine	—	—	—	—	—	—	—	—	—	—	—	—	—	—
32 Gelsemine	—	—	—	—	—	bd R	—	—	—	—	—	—	—	—
33 Hexalupine	—	—	Y ppt	—	—	Or R	—	—	—	—	—	—	—	Pk
34 Lupanine	—	—	—	—	—	—	—	—	—	—	—	—	—	—
35 Lupinine	—	—	Y ppt	—	—	—	—	—	—	—	—	—	—	—
36 Monolupine	—	—	Y ppt	—	—	Or R	—	—	—	—	—	—	—	—
37 Trilupine	—	—	Y ppt	—	—	R	—	—	—	—	—	—	—	—
38 Deltaline	—	—	—	—	—	—	—	—	—	—	—	—	—	—
39 Narcotine	—	—	—	—	—	br R	—	—	br R	—	—	—	Or R	Or R
40 Cinchonidine	—	—	—	—	—	—	—	—	—	—	—	—	lt Y	—
41 Emetine	—	—	—	—	—	—	—	—	—	—	—	—	lt Or Y	Br
42 Scopolamine	—	—	—	—	—	—	—	—	YΔ—	—	—	—	—	—

B = blue  
bd = blood  
bl = bluish  
Br = brown  
br = brownish  
ch = cherry  
Cr = crimson  
dk = dark  
dkng = darkening  
dtty = dirty

em = emerald  
fl = fluorescence  
fd = fading  
G = green  
gr = greenish  
L = lavender  
lt = light  
ol = olive  
Or = orange

CHEMICAL literature abounds with individual tests for alkaloids, but hitherto they have not been applied to all alkaloids and no systematic method for their identification has been available. The author has found that known reactions, modifications of known reactions, and new color reactions with simple reagents will enable one to identify forty-two of the more common alkaloids.

The alkaloids in Table I are to be identified in the order given. In all cases a few milligrams of each are treated at room temperature, unless otherwise directed, with a few cubic centimeters of the reagent shown in Table II, so that effects of all reagents used on these alkaloids are now determined and disclosed. (For various confirmatory tests, see especially Mercks Reagenzien-Verzeichnis, 1932.)

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of Alkaloids

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Table with 10 columns (15-23) and multiple rows of chemical test results. Includes a legend for colors (P=purple, Pk=pink, ppt=precipitate, etc.) and a list of reagents (1-23) at the bottom.

TABLE II. REAGENTS

- 1 Aqueous solution of NaOH and K3Fe(CN)6 (18)
- 2 Concentrated H2SO4 (6)
- 3 Eder's reagent: Br, KBr, H2O, 1:2:20 (22)
- 4 NH4OH.HCl in excess NaOH (11)
- 5 HCl, KClO3, and NH3 (16)
- 6 1% solution of (NH4)2VO4 in concentrated H2SO4 (10)
- 7 Aqueous KOH and H3PO4.12MoO3 (4)
- 8 o-H3PO3 (5)
- 9 1% solution of H2TiO3 in concentrated H2SO4 (15)
- 10 Fuming HNO3 and NH3 (21)
- 11 Aqueous NaOH and amyl alcohol (13)
- 12 Bromine water, Hg(CN)2, and CaCO3 (7)
- 13 Na2S2O8 and concentrated H2SO4 (14)
- 14 Concentrated H2SO4 containing 1% HNO3, PbO2 (12)
- 15 K3Fe(CN)6 in HNO3 (3)
- 16 2% solution of Na2Fe(CN)5NO, NaOH, and HCl (8)
- 17 H3PO4.12MoO3, then spot with NH3 (20)
- 18 Concentrated H2SO4 and a few mg. of MnO2 (1)
- 19 10% FeCl3 solution
- 20 Concentrated H2SO4 and a few mg. of K2Cr2O7 (17)
- 21 2% resorcinol in concentrated H2SO4 (9)
- 22 Cl, NH3, and HCl (2)
- 23 Concentrated H2SO4 and a few mg. of Ce2O3 (19)



# Correlation of Methods for Measuring Heat of Hydration of Cement

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MEASUREMENTS of heat of hydration of cement have been made extensively only during the past few years, beginning at a time when little was known about either the characteristics of heat liberation or the thermal properties of the materials involved. It is not surprising, then, that discrepancies between results from different calorimeters were encountered. The present paper is an attempt to correlate the results from different types of calorimeters and to point out the limitations and advantages of each. A brief description of each type of calorimeter is given and the sources of errors that may be involved in each are discussed. Supporting data are the result of researches conducted at the Massachusetts Institute of Technology during the past three years.

Heat of hydration of cement is important to engineers mainly because of the temperature rise that it produces in thick concrete structures. In slabs less than about 30 cm. (1 foot) thick, the temperature rise is small and heat of hydration is usually unimportant. If it is desired to compute the temperature changes that are likely to occur in a body of concrete from which some heat escapes (1), the heat of hydration is not used directly, but is first expressed in terms of the equivalent temperature rise that it would cause in the concrete if no heat were lost. A plot of the equivalent temperature rise against time is called an adiabatic time-temperature curve, which is of interest to engineers.

For the purpose of comparing cements, on the other hand, heat of hydration is best expressed directly as calories per gram of cement. The heat expressed in this way does not involve either the aggregate or the proportions employed in making the concrete. Adiabatic temperature rise of concrete can be computed from heat of hydration of cement by multiplying the latter by the weight of cement per unit weight of concrete, and then dividing the resulting product by the specific heat of the concrete. The specific heat varies with the type of aggregate and with temperature.

Four factors that affect the conversion of heat of hydration of cement into adiabatic temperature rise of concrete are (1) the immediate heat liberation, (2) the variation with temperature of the specific heat of concrete, (3) the water-cement ratio, and (4) the curing temperature. Some of these factors were overlooked when heat of hydration studies first began to be made only a few years ago. Because they are of general interest, they will be discussed before the various calorimeters are described.

## Immediate Heat Liberation of Cement

When cement is mixed (in a Dewar jar) with water of equal temperature, an appreciable temperature rise occurs almost immediately and continues at diminishing rate for a half hour or more. This temperature rise is believed to be due mainly to the solution of free oxides and impurities, and only a small amount is believed to be due either to the hydration of primary compounds or to the wetting of the cement grains. The amount of immediate heat liberation, computed from temperature rise of cement paste, is shown in Table I for a number of different cements. The amount of heat liberated up to 30 minutes varies, for the cements tested, from 1.5 to 6.3 calories per gram. The average 30-minute heat liberation is about 5 per cent of the average potential

heat of hydration (not shown) for the cements listed in Table I.

The immediate heat liberation is included in the determination of heat of hydration by the heat-of-solution method, but is apt to be missed in determinations by other methods. This is one of the factors to explain the discrepancies that were encountered when results from different types of calorimeters were compared.

## Specific Heat of Concrete

The specific heat of dry cement is almost unaffected by temperature changes within the range commonly encountered by concrete structures. Likewise, the specific heat of water is almost constant. But the specific heat of cement paste increases with temperature to an extraordinary extent. At ordinary temperatures, the specific heat of the hydrated paste is lower than the sum of the heat capacities of the amounts of water and cement contained in a gram of the paste, as would be expected if the water and cement were chemically combined. In other words, hydration reduces the specific heat of cement paste at ordinary temperatures. Because of the increase with temperature, however, the specific heat of hydrated paste may be greater than that of corresponding unhydrated paste at temperatures of about 65.56° C. (150° F.) and above.

TABLE I. IMMEDIATE HEAT LIBERATION OF CEMENTS

Cement Symbol	Type of Cement	Total Heat Liberated		
		3 min.	15 min.	30 min.
		Calories per gram		
AH	High early strength	3.5	5.2	5.6
BH	High early strength	3.5	5.3	5.9
DH	High early strength	1.1	3.3	3.7
EH	High early strength	3.1	5.2	6.3
FH	High early strength	2.7	4.1	5.0
GH	High early strength	0.6	3.0	4.0
HH	High early strength	2.5	4.2	5.1
AS	Standard	3.7	4.0	4.3
CS	Standard	1.5	2.2	2.8
JS	Standard	3.6	4.1	4.4
KP	Portland pozzuolana	0.9	1.2	1.5
LL	Low heat	3.0	3.8	4.0
MM	Modified	2.4	4.1	4.3

Accurate data on the variation with temperature of the specific heat of both neat cement and concrete were first obtained in the laboratories of the Bureau of Reclamation in Denver. Recently, further tests have been made at the Massachusetts Institute of Technology with the aid of special adiabatic calorimeters designed and constructed for this express purpose.

The specific heats of well-hydrated cement paste in two water-cement ratios are shown in Table II. Note that the increase from 21.11° to 65.56° C. (70° to 150° F.) is about 50 per cent for either water-cement ratio. The results shown are for a particular, standard cement; there appears to be some variation among cements.

The large change in apparent specific heat with temperature is believed to be due to heat absorption accompanying the decreasing affinity of hydrated cement for water as the temperature is raised. Extended research on this subject is now being conducted at the Massachusetts Institute of Technology in an attempt to obtain a more adequate explanation.

It now seems clear that the variation in specific heat of concrete with temperature is almost entirely that of the



hydrated cement and that the aggregate is not responsible; in other words, the variation is in the cement paste. In Table II, the observed specific heats of a particular concrete at various temperatures are compared with corresponding computed values on the assumption that the concrete is composed of cement paste having the measured variation in specific heat, and of aggregate having a constant specific heat. The agreement is as good as the test data, and the discrepancy that exists is in the right direction to be explained by a small increase in specific heat of the aggregate. No measurements were made on the aggregate, which was siliceous, but aggregates in general exhibit a slight increase in specific heat with rising temperature. The specific heat of limestone, for example, shows an increase of 5 per cent due to a change in temperature from 0° to 100° C.

TABLE II. SPECIFIC HEAT OF CONCRETE AND CEMENT PASTE

Temperature ° F.	Neat-Cement Paste		Observed	Concrete Computed <sup>a</sup>
	Water-cement ratio, 0.25	Water-cement ratio, 0.60		
	Calories per gram per 1° C.			
70	0.265	0.380	0.226	0.225
90	0.277	0.408	0.232	0.230
110	0.303	0.455	0.240	0.237
130	0.340	0.505	0.249	0.244
150	0.400	0.580	0.26C	0.255

<sup>a</sup> Computed on basis of 14.4 per cent of paste by weight (1 bbl. of cement per cu. yd. of concrete) and 85.6 per cent aggregate (specific heat assumed constant = 0.20).

With such variations in specific heat of cement pastes and concretes as are shown in Table II it is clear that adiabatic temperature rise of concrete cannot be translated accurately into heat of hydration of cement, or vice versa, without taking the variations into account.

Before leaving the subject of specific heat, mention should be made of one phase that remains indefinite. The specific heat of fresh concrete is the weighted-average specific heat of the ingredients. After hydration, a considerably different value prevails. Considering only the cement paste, which alone is affected by hydration, the specific heat at 21.11° C. (70° F.) is decreased by hydration to the extent of 30 to 40 per cent. A certain amount of error must be involved in assuming that the specific heat of well-hydrated paste or concrete applies at all ages. Unfortunately, it is difficult to measure the specific heat of cement paste at the early ages, when heat is still being generated at an appreciable rate.

TABLE III. EFFECT OF WATER-CEMENT RATIO ON HEAT OF HYDRATION<sup>a</sup>

Water-Cement Ratio	Heat of Hydration		
	3 days	7 days	28 days
	Calories per gram		
0.30	45.7	58.3	74.3
0.40	49.2	61.8	82.9
0.50	52.3	69.8	91.4

<sup>a</sup> Tests made by heat-of-solution method. Cement contained (potential) 7 per cent C<sub>3</sub>A and 51 per cent C<sub>3</sub>S.

Interpolation between the known hydrated and unhydrated values, in accordance with the degree of hydration, seems to offer the safest means of ensuring a reasonable degree of accuracy where specific heat is involved.

Water-Cement Ratio

Heat of hydration of cement is usually determined on a neat-cement paste of relatively low water-cement ratio. Because only a part of the water in concrete was believed to combine with the cement, it was first thought that the difference in water-cement ratio between neat paste and concrete was not important. The heat of hydration increases

appreciably with increasing water-cement ratio, however, even in the range of ratios encountered in concrete.

In Table III are given the measured heats of hydration at various ages for a standard cement in three water-cement ratios, from 0.30 to 0.50 by weight. While the effect of increasing water content is not great at the age of 3 days, it is relatively important at the later ages. Specimens of still higher water-cement ratios were prepared by slowly rotating vials of the paste during setting to prevent separation of water. The results were not consistent with those for lower water-cement ratios, where test methods were straightforward, so they were not included in the table. Auxiliary tests indicated that the rotation during setting had an effect on the hydration. Until further studies are made of the higher water-cement ratios, it is believed to be safe to extrapolate the results in Table III up to a ratio of about 0.60.

Curing Temperature

A change in curing temperature appears to affect mainly the rate of heat liberation of cement. The heat liberation at higher temperature is generally greater at early ages but about the same at later ages as at lower temperature. Heat-of-hydration results are shown in Table IV for a standard cement cured at three different temperatures. The 3-day values for curing at 4.44° and 39.44° C. (40° and 104° F.), are seen to be 29.5 and 72.3 calories per gram, respectively, a difference of about 150 per cent. But at 28 days the difference is only 8 calories, and at 90 days it is only 4 calories. Many tests have indicated greater heat liberation for lower curing temperature at later ages. This is in agreement with tests reported by Hornibrook and associates (3).

TABLE IV. EFFECT OF CURING TEMPERATURE ON HEAT OF HYDRATION

Temperature ° F.	Heat of Hydration for Water-Cement Ratio 0.40			
	3 days	7 days	28 days	90 days
	Calories per gram			
40	29.5	43.5	78.4	88.8
74	52.4	72.4	83.6	90.8
104	72.3	80.3	86.8	93.1

It is unfortunate that mass-concrete temperatures cannot be duplicated readily in the laboratory. Thus, it is necessary usually to convert heats of hydration obtained under constant temperature conditions to temperature rise of concrete curing at variable temperature. There is need for further tests aimed toward the establishing of conversion factors for variations in curing temperature.

Calorimeters

THE CALORIMETRIC PROBLEM. The measurement of heat of hydration of cement is difficult because of the great variation in the rate at which the heat is liberated. When the cement is first mixed with water, an appreciable amount of heat is liberated immediately, as described above. After the immediate heat liberation has subsided, the rate is low for a time, but as the major compounds begin to hydrate, the rate increases, first slowly and then more rapidly, until at about 8 hours for an average cement a maximum rate is reached. The maximum rate does not correspond to final set, but usually occurs later; final set is an arbitrary hardness that does not require as much hydration and heat liberation as generally occurs up to the time of the maximum rate of heat liberation. After the maximum rate is passed, there is a rapid decline in rate followed by a slower, continued decline that may bring the rate at the end of a week to only about 1 per cent of the maximum. And yet, this slow but continued heat liberation accumulates to an appreciable amount over a period of days or weeks.



The most obvious method of determining the heat of hydration of cement is to measure the temperature rise of an insulated specimen in a room of constant temperature. But even after carefully sealing the specimen against moisture loss and making correction for heat losses, reliable results can be obtained by this method only up to about 3 days. Later results are usually lacking in accuracy because the corrections are larger than the quantity being measured. Under typical conditions, one might find that a specimen of 181.44 kg. (400 pounds) weight, insulated all around with 15 cm. (6 inches) of kapok, would reach a maximum temperature at about 3 days and thereafter would decline in temperature despite its heat generation. This example illustrates the difficulty of measuring heat of hydration over a long period of time and shows that the early method, consisting of measuring temperature rise of insulated concrete, could not give satisfactory long-time results.

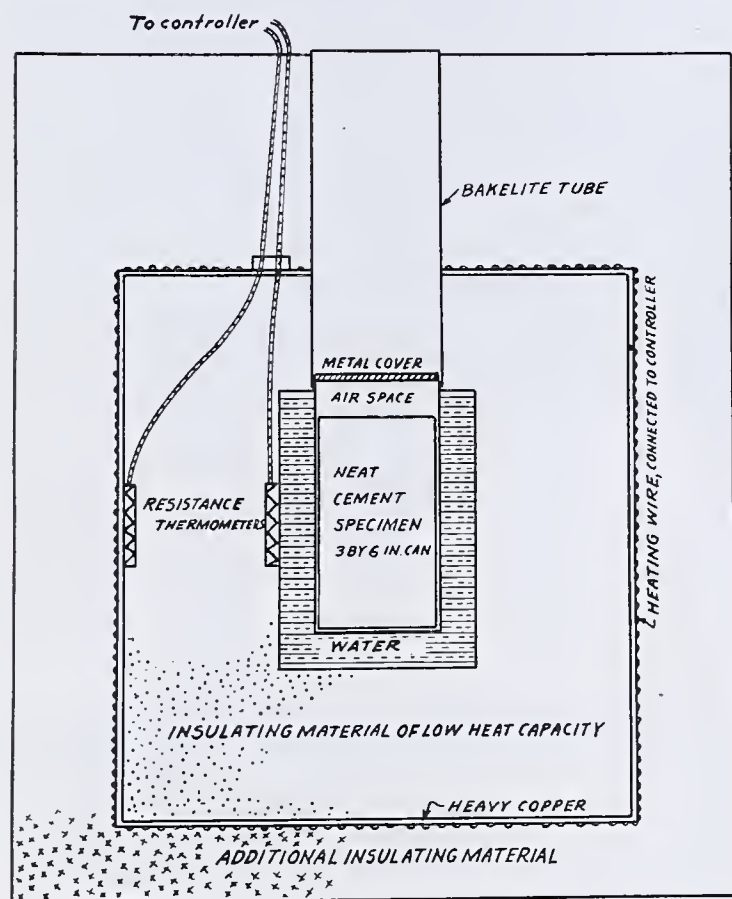


FIGURE 1. ADIABATIC CALORIMETER IN WHICH CONCRETE IS SIMULATED BY NEAT CEMENT AND WATER

**ADIABATIC CALORIMETER.** The adiabatic calorimeter avoids heat losses from a specimen of concrete by keeping the room exactly as warm as the specimen. In the most satisfactory type of adiabatic calorimeter, an automatic controller actuates heaters that maintain zero temperature difference between a thermometer in the specimen and another in the room. Temperatures are either registered by a separate recorder or are observed from time to time to provide the time-temperature curve.

An economical type of adiabatic calorimeter has recently been developed at the Massachusetts Institute of Technology. It takes advantage of the fact that the variation in specific heat of concrete is almost solely in the cement paste, and employs a concentrated neat-cement specimen to replace the bulky concrete specimen usually employed. A cross-sectional drawing of such a calorimeter is shown in Figure 1. The neat-cement specimen, weighing about 1.36 kg. (3 pounds), is surrounded by a jacket containing a measured

amount of water, sealed in metal, and thus the thermal properties of concrete are simulated. A few inches from the specimen and its water jacket is a copper container that is maintained at the same temperature as the water jacket, so that no heat can escape from the specimen.

Advantages of adiabatic calorimeters in general are: (1) the adiabatic time-temperature curve of concrete is obtained directly, (2) any type of cement can be tested, (3) the hydration temperature simulates what would develop in a heavy mass, and (4) they provide the mass-curing condition for simultaneously testing other specimens for other properties.

TABLE V. EFFECT OF CARBONATION OF TEST SAMPLES ON HEAT OF HYDRATION DETERMINED BY HEAT-OF-SOLUTION METHOD

Cement No.	Water-Cement Ratio	Age Days	Condition	CO <sub>2</sub> %	Heat of Hydration	
					Observed	Corrected for CO <sub>2</sub>
1	0.40	60	Protected	0.9	65.1	59.9
			Not protected	2.2	75.1	62.3
2	0.60	75	Protected	2.0	106.9	95.3
			Not protected	4.5	120.2	94.1
3	0.40	90	Protected	0.8	107.1	102.5
			Not protected	3.9	126.3	103.7

Disadvantages of adiabatic calorimeters are: (1) they are expensive and require close temperature control, (2) large specimens are generally required, and (3) they are not accurate for the first hour after mixing the concrete for the specimen.

**HEAT-OF-SOLUTION CALORIMETER.** Woods and his co-workers (6), realizing early that continuous observations on specimens for determining the heat of hydration would be exacting and expensive, applied the heat-of-solution method to the problem. In this method, it is necessary only to determine the difference in heat of solution of corresponding samples of cement at two ages of hydration to have the amount of heat liberated between those ages. If one of the ages is zero—in other words, if one sample is dry cement—and the age of the corresponding sample is 28 days, the difference in heat of solution of the two samples represents the total amount of heat evolved up to 28 days. A description of the heat-of-solution method in simplified form has been given by Lerch (5), and no detailed account need be given here.

Heats of hydration determined by the heat-of-solution method in most American laboratories have been too high to indicate the correct temperature rise of concrete. Also in England, tests reported by Lea (4) show the heat-of-solution method to give considerably higher values than the adiabatic method.

Sources of error not commonly considered in the heat-of-solution method are carbonation and drying of hydrated samples during preparation for testing. Of these two sources of error, carbonation is the one that makes heat-of-hydration results too high.

Carbonation of a cement sample before it is dissolved in acid reduces its heat of solution, because the heat of solution of calcium carbonate is less than that of calcium hydroxide. In the particular acid solution employed, the heat of solution of calcium carbonate (ignited basis) was found to be only 102 calories per gram as compared with 557 for calcium hydroxide. As each per cent of carbon dioxide corresponds to 1.27 per cent of transformed calcium hydroxide (ignited basis), each per cent of carbon dioxide would be expected to cause an error of  $(5.57 - 1.02) \times 1.27$  or 5.8 calories per gram. Each per cent of absorbed carbon dioxide would then be expected to reduce the heat of solution of the hydrated sample by 5.8 calories per gram. The difference between values for dry and hydrated samples would then be greater, and the heat of hydration as determined by the heat-of-solution



method would be too great by 5.8 calories per gram for each per cent of carbon dioxide absorbed by a hydrated sample.

An investigation revealed that it was common for hydrated samples to absorb more than 0.5 per cent of carbon dioxide during grinding. Dry samples were relatively unaffected by carbonation. The computed effect of carbonation was checked by testing samples carbonated to different extents. In one series of tests, one sample was protected so as to minimize carbonation and the corresponding sample was purposely carbonated more than usual during grinding. Results of such tests on three cements are shown in Table V. After applying the correction of 5.8 calories per gram for each per cent of carbon dioxide, the results are in fair agreement. The accuracy of the calorimeter was about 2 calories per gram.

It should not be concluded that the effect of carbonation is as simple as merely changing free calcium hydroxide to the carbonate. Actually, the carbonation seems to affect mainly the lime contained in the gel of the hydrated cement, and to affect but little the crystals of calcium hydroxide. Therefore, the carbonation involves another step, that of separating the lime from the gel, and this was not considered in deducing the correction value of 5.8 calories per gram for each per cent of carbon dioxide. It is indicated that the separation of a small amount of lime from the gel requires little energy and that the correction value of 5.8 calories is therefore approximately correct where small amounts of carbon dioxide are involved.

Turning to the effect of drying of hydrated samples during preparation for test, an error in the opposite direction is encountered. Any extensive drying of a hydrated sample would be expected to increase its heat of solution and hence the heat of hydration obtained by this method would be too small. If this fact is realized, samples can readily be prepared without drying to the point of introducing appreciable error. Drying at 50° C., for example, was found to increase the heat of solution by 3 calories per gram, while drying at 110° C. caused an increase of about 16 calories per gram. Ordinarily, drying to the equivalent of 50° C. is not encountered, although this amount of drying can be obtained at room temperature when the humidity is low.

The factors to be borne in mind in determining equivalent temperature rise of concrete from heat-of-solution results are as follows:

1. Heat of hydration values are often reported on ignited basis (making values too high).
2. Carbonation of hydrated samples may have occurred (making values too high).
3. Drying of hydrated samples may have occurred (making values too low).
4. Lower water-cement ratios are generally used for heat-of-solution specimens than for concrete (making values too low).
5. Immediate heat of hydration is included in heat of solution.
6. Specific heat of concrete varies with temperature.
7. Temperature of curing test specimens is usually lower than that of concrete.

The advantages of the heat-of-solution calorimeter are that small neat-cement specimens may be used and that the specimens require no attention other than temperature control between tests. Disadvantages are that a high degree of accuracy is necessary in the measurement of heats of solution to get fair accuracy in heat of hydration, and that some cements, particularly Portland pozzuolana cements, do not dissolve quickly enough in acids to be tested by the heat-of-solution method. The seven factors listed above are not considered to be disadvantages of the method, because they can be eliminated or corrected.

VANE AND CONDUCTION CALORIMETERS. Reliable results cannot be obtained on highly insulated neat-cement speci-

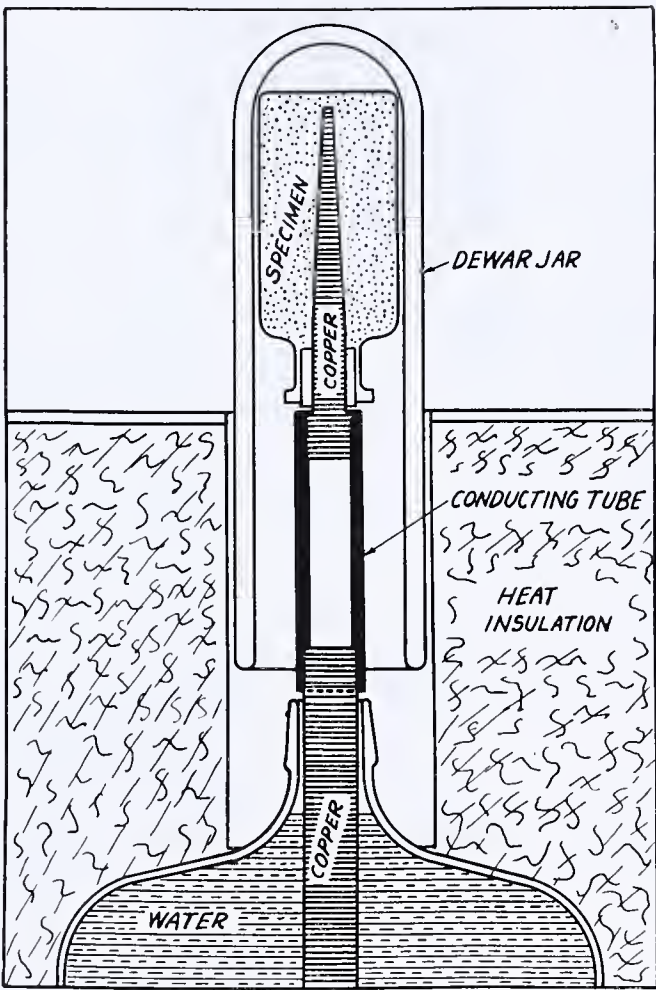


FIGURE 2. CONDUCTION CALORIMETER

mens because abnormally high temperatures develop that not only affect the heat of hydration but make even high insulation inadequate. The vane calorimeter (2) employs neat-cement specimens but avoids high temperatures by conducting the heat away through metal vanes almost as fast as it is liberated. The rate at which the heat is conducted away is determined by measuring accurately the small temperature difference that develops between the specimen and the outer edge of the vanes. When a continuous record of the rate of heat removal from the specimen is obtained, the total amount of heat removed up to any age can be computed. Because the specimen varies so little in temperature that only a small amount of heat is stored in the specimen, the total amount of heat removed is the heat of hydration.

A modification of the vane calorimeter is the "conduction" calorimeter, exactly the same in principle but with a metal tube replacing the vanes. Figure 2 presents a cross section of the conduction calorimeter, showing how heat is removed from the specimen by a tapered copper rod and how substantially all heat is caused to flow in the direction of the metal tube by reason of a surrounding Dewar jar. Thermometers, not shown in the figure, are at either end of the conducting tube. The advantages of the conduction over the vane calorimeter are (1) greater accuracy, (2) use of smaller specimens, and (3) a more faithful response to changes in rate of heat liberation.

The advantages of vane and conduction calorimeters as a type are: (1) early heat liberation can be studied in detail, (2) any cement can be tested, and (3) continuous results up to about 7 days can be obtained at low cost. Disadvantages are that results are lacking in accuracy after about 7 days and that curing conditions are practically limited to a substantially constant temperature.



### Comparison of Results from Different Calorimeters

Comparable tests, employing the three types of calorimeters described above, indicated that almost identical results could be obtained from all three calorimeters when due regard was paid to possible sources of error. Results of heat-of-solution tests made on neat specimens cured on the time-temperature curve of corresponding concrete, when converted into temperature rise of concrete, closely represented the time-temperature curve obtained from an adiabatic calorimeter. Likewise, results of heat-of-solution tests on neat specimens cured at 21.11° C. (70° F.) checked very well with results on similar neat specimens tested in vane calorimeters at 21.11° C. (70° F.). Results were not in agreement, however, until proper account was taken of (1) immediate heat of hydration, (2) carbonation of heat-of-solution specimens, (3) water-

cement ratio, and (4) variations in specific heat of concrete with temperature. The effects of the other possible sources of error discussed above either were not involved in the comparisons or were too small to be subject to proof of validity in the tests that were made.

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## Separation of the Chrysanthemum Carboxylic Acids

### Destructive Effect of Steam Distillation on Chrysanthemum Monocarboxylic Acid

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THE acid methods of estimating the pyrethrin I and II content of pyrethrum flowers and their extracts depend upon the separation of the chrysanthemum acids by steam distillation of the steam-volatile monocarboxylic acid (5, 6, 7). Estimations of pyrethrin I by these methods are usually lower than those obtained by difference after estimation of total pyrethrins by the Gnadinger-Corl (1) reduction method and of pyrethrin II by the Haller-Acree (4) methoxyl method.

TABLE I. LOSS OF CHRYSANTHEMUM MONOCARBOXYLIC ACID ON REPEATED STEAM DISTILLATION OF THE SAME SAMPLE

Operation	Acid in Distillate	(Acid expressed as cc. equivalent of 0.0200 <i>N</i> base)		Total Loss %	Acid in Residue
		Loss %			
1	52.0	..	9.1	9.1	0.0
2	47.3	4.7	9.1	18.3	0.1
3	42.5	4.8	10.2	26.8	0.05
4	38.0	4.5	10.6	35.2	0.1
5	33.5	4.5	11.8	43.0	0.1
6	29.6	3.9	11.6	50.4	0.1
7	25.8	3.8	12.8	56.9	0.05
8	22.2	3.6	13.9	61.4	0.1
9	20.1	2.1	9.5	64.0	0.1
10	18.8	1.4	7.0	66.5	0.1
11	17.4	1.3	6.9	69.0	0.1
12	16.1	1.3	7.5		

Graham (2) has found that steam distillation of perfumed oil extracts to remove the essential oil (as directed in the Seil method, 6) results in a 25 per cent loss of pyrethrin I, and (3) that there is a lack of uniformity among the results of different analysts. This study was undertaken to show the effect of steam distillation on chrysanthemum monocarboxylic acid and to develop a different method of separating the acids.

### Procedure

A sample of pure chrysanthemum monocarboxylic acid (b. p., 140–2° at 9 mm.) was subjected to repeated steam distillations—the acid after extraction from the distillate and

titration with standardized base was reacidified and steam-distilled again. All steam distillations were carried out as directed by Seil. After eleven steam distillations (Table I) 69 per cent of the original acid present was destroyed. The average loss for each distillation was over 10 per cent.

A series of samples containing various amounts of the chrysanthemum monocarboxylic acid was prepared both by direct weighing of the pure acid and by measuring off aliquots from a standardized alkaline solution of the acid. Each sample was steam-distilled and the acid reestimated as in the Seil method. The results of a series of determinations are condensed in Table II.

It is evident that steam distillation destroys an average of over 10 per cent of the chrysanthemum monocarboxylic acid; consequently, all methods of estimation of the pyrethrins involving steam distillation give low values for pyrethrin I.

TABLE II. LOSS OF CHRYSANTHEMUM MONOCARBOXYLIC ACID ON STEAM DISTILLATION OF VARIOUS SAMPLES

Sample	(Acid expressed as cc. equivalent of 0.0200 N base)		Acid in Residue
	Acid Present	Acid in Distillate	
		Loss %	
A	31.9	27.5	4.4 13.8 0.1
B	37.6	34.5	3.1 8.2 0.1
C	36.0	31.8	4.2 11.6 0.0
D	33.3	28.6	4.7 14.1 0.1
E	36.6	32.0	4.6 12.6 0.1
F	38.3	32.8	5.5 14.4 0.1
G	36.9	31.5	5.4 14.6 0.1
H	43.8	39.4	4.4 10.0 0.0
I	43.9	37.6	6.3 14.6 0.1
J	48.2	43.8	4.4 9.1 0.1
K	33.4	28.5	4.9 14.6 0.1
L	41.0	35.0	6.0 14.6 0.1

That any degree of precision is possible in the acid methods of pyrethrin analysis can be explained by the fact that under comparable conditions the loss of the monoacid on steam distillation is approximately proportional to the amount of acid present. The lack of agreement in the results of different analysts is also understandable.



Method of Separation

In the course of analyses for the pyrethrins by the Seil method it was observed that low-boiling petroleum ether does not extract the chrysanthemum dicarboxylic acid from an acidified solution. Since the chrysanthemum monocarboxylic acid is soluble in petroleum ether, it should be possible to separate the mono- from the dicarboxylic acid by such a selective extraction. A few preliminary experiments were sufficient to demonstrate that petroleum ether does not extract the dicarboxylic acid; but, in order to prove that it is possible to separate the two acids, several artificial mixtures of the two acids were prepared and subjected to the following analysis:

Aliquots from standardized, freshly prepared, alkaline solutions of the acids were mixed, acidified, and then extracted with low-boiling petroleum ether as in the Seil method, with the exception that care was taken to retain quantitatively the water layer and washings. The petroleum ether extract was titrated with standardized 0.0200 *N* base in the usual manner, but the water layer was again retained. The acidified water layer and washings from the petroleum ether extraction were then extracted with diethyl ether, and the chrysanthemum dicarboxylic acid was determined by the Seil method. The acids were then recombined and the mixture was subjected to analysis for both acids by steam distillation (the Seil method).

TABLE III. SEPARATION OF CHRYSANTHEMUM MONO- AND DICARBOXYLIC ACIDS

(Both acids expressed in cc. equivalent of 0.0200 <i>N</i> base)							
Sam- ple	Acid Present		Acid Found				Loss by Steam Dis- tillation, Mono- %
			Selective Solvent Extraction		Steam Distillation		
	Mono-	Di-	Mono-	Di-	Mono-	Di-	
A	29.0	39.8	29.2	39.7	25.2	40.2	13.1
B	34.1	41.9	34.2	41.8	30.3	42.1	11.3
C	38.7	81.4	38.7	81.2	32.6	81.7	16.0
D	45.5	40.4	45.6	40.3	41.4	40.6	9.0
E	38.4	41.9	38.5	41.8	36.0	42.0	6.3
F	0.0	44.0	0.1	44.0	0.1	44.1	..
G	33.1	0.0	33.1	0.1	30.0	0.1	9.4
H	35.2	49.8	..	..	31.6	49.9	10.3

Several such determinations were carried out, and the results are summarized for comparison in Table III. It is apparent that the separation of the two acids by the selective solvent extraction method is quantitative, well

within the experimental errors involved. The destructive effect of steam distillation on the monocarboxylic acid is again demonstrated; for, while the results of the two methods for the dicarboxylic acid are comparable, those for the monocarboxylic acid differ by over 10 per cent. The use of this method for the estimation of the pyrethrin content of pyrethrum flowers and its extracts was suggested. But, when it was applied to samples prepared in accordance with the Seil method, the results were somewhat high for both acids, perhaps because of the presence of other acidic constituents. Further work is being pursued, and there are indications of a successful solution. Selective extraction of the monoacid by other solvents is also being investigated.

Conclusion

Because of the destructive effect of steam distillation on the chrysanthemum monocarboxylic acid, the acid methods of pyrethrin I analysis are inaccurate and unreliable (8). It is possible to separate the two chrysanthemum acids by the selective extraction of the monocarboxylic acid with low-boiling petroleum ether, but this method requires further study before it can be applied to the estimation of the pyrethrin content of pyrethrum flowers and their commercial extracts.

Acknowledgments

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Evaluation of Commercial Arsenious Oxide by Titration with Iodine

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THE following procedure has been used in the analysis of commercial arsenic trioxide:

Weigh out samples of 5.000 grams, cover with 70 ml. of 6 *N* sodium carbonate solution, and boil until completely dissolved. Cool, make up to 1 liter, and take a 50-ml. aliquot for the analysis. Make the solution barely acid with 6 *N* sulfuric acid, add 3 grams of sodium bicarbonate, and titrate with 0.1 *N* iodine to a starch end point.

TABLE I. ANALYSIS OF ARSENIC TRIOXIDE  
(95 to 97 per cent pure As<sub>2</sub>O<sub>3</sub>)

	%	%	%	%
1 Probable purity	97.40	96.44	95.79	95.06
2 Direct titration value	97.82	97.01	96.58	95.48
3 Artificial standard	97.40	96.50	96.00	95.07
4 100 - (nonvolatile + As <sub>2</sub> O <sub>5</sub> + SO <sub>3</sub> )	97.40	96.34	95.89	95.28
5 Nonvolatile residue	1.78	3.01	3.27	3.96
6 As <sub>2</sub> O <sub>5</sub>	0.32	0.20	0.34	0.31
7 SO <sub>3</sub>	0.50	0.45	0.50	0.45
8 Sb <sub>2</sub> O <sub>3</sub>	0.50	0.46	0.55	0.78
9 Se	0.16	0.21	0.17	0.21

If the iodine solution is standardized in exactly the same way against a sample of arsenic trioxide known to be pure, the results are very exact, provided nothing other than arsenic is present that is oxidized by iodine. It has been known for some time, however, that the values thus obtained are usually too high. The experiments described in this paper were undertaken to ascertain the reason for the error and to see if the difficulty could not be overcome in some simple manner.

In Table I, the results obtained in the analysis of four samples containing 95 to 97 per cent of arsenic trioxide are given. The first horizontal column gives the actual purity of the sample obtained by determining all the impurities known to be present and subtracting the sum of these values from 100. The second column gives the values obtained by direct titration as outlined above; these values are about 0.5 per cent too high. The third column gives values which were



obtained by standardizing the iodine solution against pure arsenic trioxide, to which the impurities found to be present in the sample to be analyzed had been added intentionally. The fourth column gives values obtained by adding together the nonvolatile, arsenic pentoxide, and sulfur trioxide contents and subtracting this value from 100.

These results show clearly that the values obtained by direct titration are about 0.5 per cent too high. Good results were obtained, however, by standardizing the 0.1 *N* iodine against pure arsenic trioxide to which impurities had been added intentionally, or by subtracting the nonvolatile residue plus arsenic pentoxide plus sulfur trioxide from 100 per cent.

TABLE II. ANALYSIS OF ARSENIC TRIOXIDE  
(98 to 99 per cent pure  $\text{As}_2\text{O}_3$ )

	%	%	%	%
1 Probable purity	98.50	97.90	98.60	98.42
2 Direct titration value	98.88	98.40	98.86	99.04
3 Artificial standard	98.42	97.93	98.30	98.60
4 100 - (nonvolatile + $\text{As}_2\text{O}_5$ )	98.26	97.79	98.45	98.59
5 Nonvolatile	1.00	1.10	0.87	0.059
6 $\text{As}_2\text{O}_5$	0.74	1.11	0.68	0.082
7 $\text{Sb}_2\text{O}_3$	0.23	0.19	0.23	0.025
8 Se	0.056	0.044	0.027	0.25

Table II gives results obtained in the analysis of samples of 98 to 99 per cent purity. Here again, the values obtained by direct titration are about 0.45 per cent too high on an average, but the results are good if the iodine solution is

standardized against arsenic trioxide to which the same impurities have been added.

TABLE III. ANALYSIS OF ARSENIC TRIOXIDE  
(90 to 91 per cent pure  $\text{As}_2\text{O}_3$ )

	%	%	%	%	%
1 Probable purity	89.89	90.35	91.15	89.65	90.57
2 Direct titration value	90.49	91.61	92.42	90.25	89.94
4 100 - (nonvolatile + $\text{As}_2\text{O}_5$ + $\text{SO}_2$ + S)	90.29	90.31	92.15	90.25	90.81
5 Nonvolatile residue	7.22	6.41	5.20	7.95	7.35
6 $\text{As}_2\text{O}_5$	0.40	0.15	0.21	0.15	0.30
7 $\text{SO}_2$ + sulfide S	2.09	3.13	2.44	1.65	1.54
8 $\text{Sb}_2\text{O}_3$	1.00	0.97	1.47	0.63	0.86
9 Se	0.55	0.41	0.45	0.39	0.48

In Table III, the results obtained in the analysis of samples of arsenic trioxide which were 90 to 91 per cent pure are given. Here the results obtained by direct titration are erratic. In two cases the results are 1.25 per cent too high but in one case the value is 0.63 per cent too low. These samples contain appreciable quantities of selenium dioxide, antimony trioxide, and sulfur trioxide + sulfides. They were hard to titrate and the end points were not easy to find. In samples of this character, the only thing to do is to determine the total arsenic (by distilling as arsenic trichloride and titrating the neutralized distillate with iodine) and to make a separate determination of arsenic pentoxide. The arsenic trioxide can then be found by difference.

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## Chemical Determination of Quartz (Free Silica) in Dusts

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IN THE Knopf method (1) for the determination of quartz in the presence of silicates, the silicates are dissolved in hydrofluosilicic acid, leaving behind a residue containing quartz. The acid, however, decomposes quartz also with a resulting average rate of loss of 0.7 per cent per day of the original weight of quartz present in the sample. Knopf (1) notes that "by using the above factor of error it is possible to compute at the end of an analysis the maximum possible loss in weight of quartz originally present, thus obtaining a maximum figure of quartz." Similarly, in a more recent method (2) which proposes the use of fluoboric acid in place of hydrofluosilicic acid, Line and Aradine state that "the free silica content of the residue must be corrected for the amount of free silica dissolved during the time required to decompose the silicate. The correction factor is 0.34 per cent per day." Neither of the above methods indicates the manner in which its respective correction factors are to be applied. Accordingly, the following mathematical treatment is presented for the interest of individuals routinely using these methods of analysis.

The problem involves an application of the frequently encountered compound interest law, also called the law of organic growth, or the snowball law, which may be expressed for rates of decrease by the differential equation  $dy/dx = -ky$ . This expression is the first derivative of the exponential equation  $y = y_0 e^{-kx}$ , or in the logarithmic form

$$\log y = \log y_0 - kx \log e$$

In the present problem

$$\begin{aligned} y &= \text{mg. of quartz in residue} \\ y_0 &= \text{mg. of quartz originally present} \\ k &= \text{rate of loss (0.7 per cent per day in the Knopf method)} \\ x &= \text{time of action in days} \\ \log e &= 0.43429 \end{aligned}$$

For example, in a determination of quartz in the presence of refractory silicates by the Knopf method, 500 mg. of dust required 10 days of treatment with hydrofluosilicic acid, leaving a residue corresponding to 50 mg. of quartz. The amount of quartz originally present was calculated in the following manner:

$$\begin{aligned} \log y_0 &= \log y + kx \log e \\ &= \log 50 + (0.007 \times 10 \times 0.43429) \\ &= 1.72937 \\ y_0 &= 53.63 \text{ mg. of quartz originally present, corresponding to 10.7 per cent of quartz in the original sample of dust taken for analysis.} \end{aligned}$$

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# Determination of Forms of Sulfur in Insoluble Residues from Hydrogenated Coal

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THE purpose of this paper is to describe a procedure for determining the forms of sulfur in insoluble residues obtained from hydrogenation of coal, and to give a trend of behavior of sulfur during hydrogenation. For many years sulfur has played an important role in the use of coal (3), but in the present-day industrial use it is more important than ever to know not only the sulfur content but also its various forms and distribution.

Powell and Parr (7) developed a procedure for Illinois coal and showed that the principal forms of sulfur are sulfate, pyritic, and organic. Later Powell (5) analyzed representative coals of the United States. This scheme of analysis was used in analyzing the insoluble residues from hydrogenated coal. These residues were obtained from Fisher and Eisner (2), part of whose work has covered Pittsburgh bed coal from the Bureau of Mines Experimental Mine, Bruceton, Pa. Their charge for hydrogenation was 100 grams of coal, 100 grams of tetrahydronaphthalene, and 1 gram of stannous sulfide. The initial hydrogen pressure was 703,100 kg. per sq. meter (1000 pounds per square inch) with varying time and temperature.

TABLE I. FORMS OF SULFUR IN INSOLUBLE RESIDUES

Residue	Ash %	Sulfide Sulfur % <sup>a</sup>	Sulfate Sulfur %	Pyritic Sulfur %	Organic Sulfur %	Total Sulfur Calcd. %	Total Sulfur Detd. %
1	12.7	0.57	0.95	0.14	0.16	0.70	1.95
2	27.3	1.51	2.30	0.12	0.14	0.63	3.19
3	30.0	1.73	2.60	0.18	0.18	0.60	3.56
4	52.8	3.76	5.30	0.61	0.16	0.39	6.46
Coal <sup>b</sup>	6.4	..	..	0.06	0.84	0.72 <sup>c</sup>	..

<sup>a</sup> Corrected for sulfur in 1 gram of catalyst (SnS added).  
<sup>b</sup> Original coal, moisture-free basis.  
<sup>c</sup> Calculated by subtracting sum of sulfate and pyritic from total sulfur.

The analyses showed small amounts of sulfate and pyritic sulfur, which indicated that the greater portion of the sulfur was apparently in the organic form. However, on the initial extraction with dilute hydrochloric acid, hydrogen sulfide was evolved. Later, quantitative determinations showed that most of sulfur was present as hydrochloric acid-soluble sulfides and that the organic sulfur, as determined by the standard method, was erroneously high. A procedure was then formulated by combining Powell's method for forms of sulfur in coal (5) with his method for forms of sulfur in coke (6) to determine directly sulfide, sulfate, pyritic, and organic sulfur.

### Procedure

**SULFIDE SULFUR (EVOLUTION METHOD, 4).** The 60-mesh residue (0.500 gram) was placed in a 300-cc. Erlenmeyer flask fitted with a two-hole rubber stopper. A separatory funnel was inserted in one hole, and in the other, a glass delivery tube leading to the bottom of a 300-cc. tall-form beaker, containing 30 cc. of ammoniacal cadmium chloride (30 grams of CdCl<sub>2</sub> in 300 cc. of water added to 800 cc. of water and 1200 cc. of ammonium hydroxide) and 200 cc. of distilled water. To the flask containing the residue, 60 cc. of dilute hydrochloric acid (1 part of acid and 1 part of water) were added slowly to permit even bubbling through the cadmium chloride solution. The flask was heated to boiling, and slowly boiled until all the hydrogen sulfide had been expelled by the steam. The cadmium chloride solution containing the cadmium sulfide was cooled to room temperature in ice water, acidified with 30 cc. of concentrated hydrochloric acid, and titrated with standardized iodine, using starch as an indicator. Blanks were run on the reagents used.

**SULFATE SULFUR.** The contents of the flask from the sulfide determinations were washed onto a filter and washed six times

with cold water. The residue was saved for the pyritic sulfur determination. To the filtrate in a 250-cc. beaker 20 cc. of saturated bromine water were added. The filtrate was heated to boiling, and while hot was made alkaline with dilute ammonium hydroxide (1 part of concentrated ammonium hydroxide to 1 part of water); the precipitate containing the iron was filtered off and washed. The filtrate was neutralized with concentrated hydrochloric acid and 1 cc. excess added and heated to boiling, 10 cc. of hot barium chloride (10 per cent) being added. The barium sulfate was allowed to settle overnight, filtered on an ashless filter paper, ignited at 900° C., and weighed.

**PYRITIC SULFUR.** The residue on the filter paper from the sulfate determination above was placed in a 250-cc. beaker, the filter paper was shredded with a stirring rod, and 100 cc. of dilute nitric acid (1 part of nitric acid, specific gravity 1.42, to 3 parts of water) were added and allowed to digest, with occasional stirring, at room temperature for 24 hours. The contents were placed on a filter and washed six times with cold water. The residue was saved for the organic sulfur determination. To the filtrate 5 cc. of dilute hydrochloric acid (2 parts of concentrated hydrochloric acid to 1 part of water) were added and evaporated to dryness on the steam bath. This residue was dissolved in 5 cc. of concentrated hydrochloric acid and diluted with 30 cc. of water. The iron was precipitated with dilute ammonium hydroxide and removed by filtration. The sulfur in the filtrate was determined as under sulfate sulfur above.

**ORGANIC SULFUR.** The residue from the pyritic sulfur determination was dried and the filter paper shredded; it was intimately mixed with 5 grams of Eschka mixture and covered with 5 grams more of Eschka mixture in a 30-cc. porcelain crucible. The crucible was placed in a cold electric muffle, heated to a dull-red heat for 15 minutes, and cooled. The contents were mixed well in the crucible, covered with 2 grams of Eschka mixture, and again heated in an electric muffle to 800° C. for 1.5 hours. After cooling, the contents of the crucible were washed into a 250-cc. beaker, 10 cc. of saturated bromine water were added and made acid with concentrated hydrochloric acid and filtered, and the residue was washed with hot water. The sulfur in the filtrate was determined as under sulfate sulfur above. Blanks were run on reagents used.

**TOTAL SULFUR.** The total sulfur was determined by the standard Eschka method (1).

Table I gives the results, on the percentage basis, obtained when the modification of the standard sulfur forms method is applied to the insoluble residues. Residues 1, 2, 3, and 4 represent increasing degrees of liquefaction of the coal as shown by the ash content (2). The accuracy of the procedure is shown by comparing the calculated total sulfur with the determined total sulfur. The calculated total sulfur is the sum of the sulfide, sulfate, pyritic, and organic sulfur. It is evident that unless the sulfide sulfur is determined, the organic sulfur will be erroneously high.

TABLE II. FORMS OF SULFUR IN INSOLUBLE RESIDUES

Residue	Residue Found Grams	Sulfide Sulfur Gram <sup>a</sup>	Sulfate Sulfur Gram	Pyritic Sulfur Gram	Organic Sulfur Gram	Total Sulfur Gram
1	55.7	0.32	0.53	0.08	0.09	1.09
2	26.8	0.41	0.62	0.03	0.04	0.86
3	24.3	0.42	0.63	0.04	0.04	0.86
4	13.8	0.52	0.73	0.08	0.02	0.88

<sup>a</sup> Corrected for sulfur from catalyst (SnS).

Table II gives some trends on the behavior of the sulfur during hydrogenation. From the total residue found, the grams of the various forms were calculated. This does not give a complete sulfur balance, because some of the sulfur is in the gases and some in the liquid fraction. The third column in Table II gives the sulfide sulfur corrected for the sulfur from



the catalyst (SnS), which was added. The amount of sulfide sulfur increases with the time of hydrogenation, while the pyritic and organic decrease. The pyritic sulfur may be high, because it is determined directly from the nitric acid extraction and may contain some of the organic sulfur. Residue 1 (least hydrogenated) has a much higher total sulfur content than residues 2, 3, and 4, which have almost the same amount of sulfur; yet residue 4 (13.8 grams) has about the same amount (0.88 gram) as residue 2 (26.8 grams) which has 0.86 gram.

The sulfate sulfur is shown to be erratic by the data in Tables I and II. Since residue 4 had been standing in the laboratory considerably longer than the others and had a higher percentage of sulfate sulfur, it was suspected of having gained at the expense of the sulfide sulfur.

The writers wish to thank C. H. Fisher and Abner Eisner of

the Organic Laboratory for providing the insoluble residues for this work.

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RECEIVED May 3, 1938. Presented before the Division of Gas and Fuel Chemistry at the 95th Meeting of the American Chemical Society, Dallas, Texas, April 18 to 22, 1938. Published by permission of the Director, Bureau of Mines, United States Department of the Interior. (Not subject to copyright.)

## Determination of Small Quantities of Methyl Bromide in Air

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**A method is proposed for the determination of methyl bromide in air of fumigated spaces. The procedure involves saponification of the methyl bromide by alcoholic potassium hydroxide, removal of the alcohol, oxidation of the bromide to bromate by sodium hypochlorite, and iodometric titration of the bromate. Results are reported of analyses of 13 samples ranging from 0.0480 to 0.0065 gram. The average error is -1.7 per cent; the greatest error is -3.5 per cent.**

THE discovery that methyl bromide is an effective fumigant for a number of insects and is at the same time relatively innocuous to plant tissues has resulted in a good deal of experimental work with this compound by entomologists. Consequently, the need has arisen for a method of determining methyl bromide in the air of fumigated spaces, and it is the purpose of this paper to present such a method.

There is little information in the literature bearing directly on the determination of methyl bromide. Nuckolls (5) determined the concentration of alkyl halides, including methyl bromide, in air by condensation with liquid air and subsequent pressure measurements at the original temperature. Glaser (2) reported determining the methyl bromide content of air in a refrigerator factory by drawing 100 liters of air through sodium methylate solution, then acidifying and titrating with 0.01 *N* silver nitrate and ammonium thiocyanate. The Dow Chemical Company (1) has proposed a method which involves saponification of the methyl bromide with alcoholic potassium hydroxide solution and subsequent titration with standard silver nitrate solution, using dichlorofluorescein as an adsorption indicator.

A number of samples of methyl bromide were analyzed in this laboratory by the Dow method, but with small samples the end point was very unsatisfactory. The procedure to be described is more time-consuming, but the end point is much sharper and easier to detect. Oxidation of the bromide to bromate also introduces a sixfold magnification in the results, which further contributes to the accuracy.

After saponification with alcoholic potassium hydroxide, the bromine of methyl bromide is in the form of potassium bromide. The alcohol can be removed readily and an aqueous solution obtained which contains potassium bromide and excess potassium hydroxide. Leipert and Watzlawek (3) have described a method, based on earlier work by van der Meulen (4), for the microanalytical determination of bromine in organic substances which consists essentially in combustion of the substance in oxygen, absorption of the combustion products in aqueous sodium hydroxide solution, and subsequent oxidation of the bromine to bromate. The oxidation and titration processes were easily adapted to a larger scale for the present purpose.

The method of analysis to be described involves passing air containing methyl bromide through heated alcoholic potassium hydroxide solution to produce saponification. The mixture is diluted with water and the alcohol removed by distillation. The bromide is then oxidized to bromate by sodium hypochlorite in slightly acid solution, the excess hypochlorite removed, potassium iodide added, and the iodine titrated with standard sodium thiosulfate solution.

### Apparatus

A special saponification apparatus is required, which is shown in Figure 1. (This is a slight modification of an apparatus described in a private communication from the Dow Chemical Company.) The glass tubing is 6 mm. in diameter except for portion *EE*, which is capillary tubing of about 1-mm. diameter. The bulbs are 3 cm. in diameter except for the three at the bottom, whose diameter is 2.5 cm. A tin can of suitable dimensions, covered with thin asbestos, is used for the jacket, *D*, which is held in place by a rubber stopper at *F*. A piece of cardboard is used



to extend the jacket above the side arm. There is a 10/30 female standard taper connection at *A* for attaching the sampling bulbs.

Air-sampling bulbs were made from pieces of Pyrex tubing 7 cm. in diameter and 50 cm. long, drawn down on the ends and sealed to stopcocks ground for high vacuum. A 10/30 male standard taper connection was sealed on at one end. These bulbs, which had a capacity of approximately 2 liters, were highly evacuated and tested for leaks over a period of several days. Samples were taken by evacuating a bulb and then opening one of the stopcocks to the fumigated air.

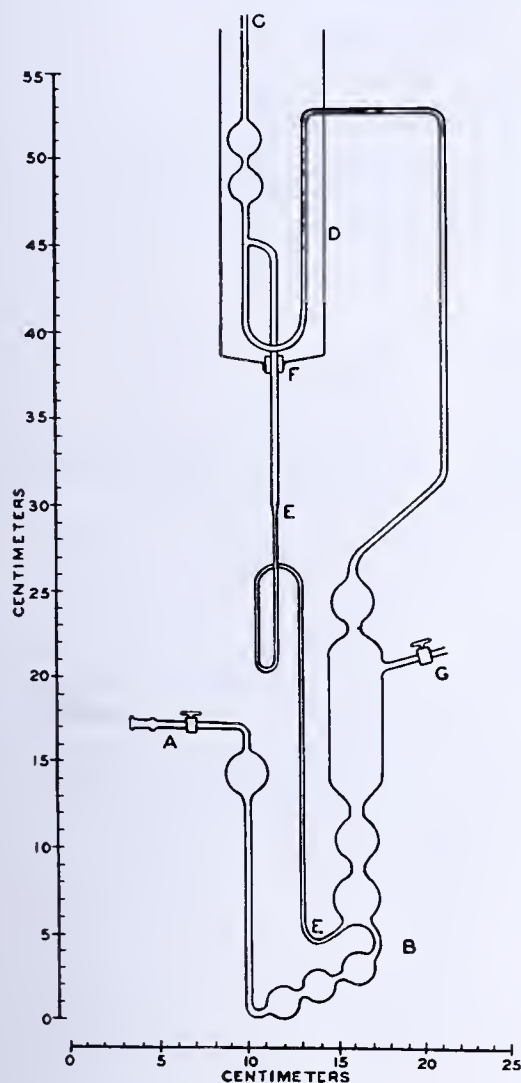


FIGURE 1. SAPONIFICATION APPARATUS

The device shown in Figure 2 was made for the introduction of weighed samples of methyl bromide into the saponification apparatus. It was fabricated mainly from a 24/40 standard taper ground-glass joint, *K, K'*; a 10/30 connection at *H* fits the saponification apparatus, and an indentation at *I* holds the sample capsule in place. *M* is a glass rod which slides through the rubber slip joint, *N*. The rod is flattened and slightly indented on the inner end.

Small glass capsules to contain samples were made of the shape shown in *O* of Figure 2.

### Reagents

Ethyl alcoholic solution of 20 grams of reagent-quality potassium hydroxide per liter.

Diethyl ether.

Solid carbon dioxide.

Solution of sodium hypochlorite made by absorbing 7 grams of chlorine in 100 ml. of 12 per cent aqueous solution of reagent-quality sodium hydroxide.

Reagent-quality sodium chloride.

Reagent-quality boric acid.

A 10 per cent aqueous solution of reagent-quality sodium formate.

Reagent-quality potassium iodide.

A 5 per cent aqueous solution of ammonium molybdate.

A standardized solution of sodium thiosulfate, approximately

0.1 *N* or 0.05 *N*, depending upon the size of the methyl bromide sample.

Starch indicator solution.

2 *N* hydrochloric acid.

Methyl bromide obtained by fractional distillation of the commercial product. After considerable low-boiling material, probably wet, had been collected, the fraction boiling at 3.4° to 3.6° C. was retained for use. Samples of this were sealed and weighed in the glass capsules previously mentioned.

### Experimental Procedure

Twenty-five milliliters of the alcoholic potassium hydroxide solution and 10 ml. of ether were introduced into the saponification apparatus through stopcock *G*. This stopcock was then closed, but the one at *A* was left open. Jacket *D* was filled with small lumps of solid carbon dioxide and was kept filled throughout the saponification. One of the sample capsules was placed in the sample adapter of Figure 2 and held in place by the glass rod. The sample adapter was then connected to the saponification apparatus. A compressed-air line was attached to stopcock *L*, and air was passed through the apparatus at the rate of 3 bubbles per second. The three bulbs at the bottom of the saponification apparatus were immersed in a water bath so that water covered the bulbs but did not reach capillary tube *E*. The bath was kept at 68° C., a temperature that caused the ether to siphon down through the capillary tube about once every minute or two but did not cause any loss of ether vapor at *C*.

While the water bath was heating, solid carbon dioxide was packed around the portion of the sample adapter where the sample lay and was kept there for at least 10 minutes. The sample was thus cooled so that it would not evaporate instantaneously when the capsule was broken. When the ether was siphoning regularly and the sample was well chilled, the capsule was broken by glass rod *M* and the solid carbon dioxide was removed from around the sample. The rate of evaporation of methyl bromide was controlled, when necessary, by the application of solid carbon dioxide, so that about 20 minutes were required for complete evaporation. The stream of air was then continued for one hour. The stopcock at *A* was then closed and the apparatus taken down. After the solid carbon dioxide had been removed from the jacket, the saponification apparatus was rinsed thoroughly with distilled water.

The combined washings were put in a 500-ml. round-bottomed flask, distilled water was added to make the volume about 250 ml., and distillate was removed until it gave no more than an extremely faint iodoform test. Water was added occasionally so that the final volume was about 150 ml. Removal of the alcohol is necessary to avoid reduction of the sodium hypochlorite that is added later.

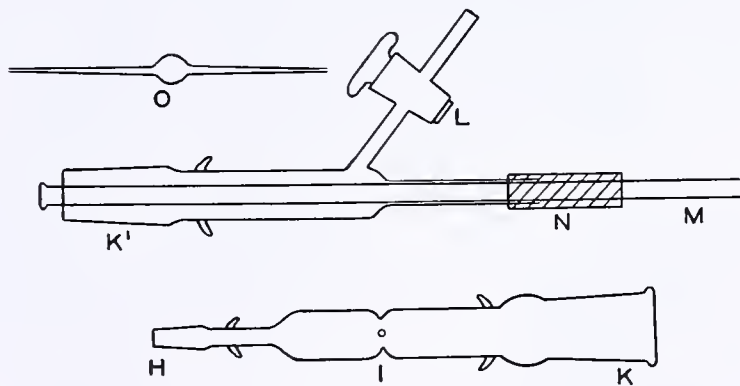


FIGURE 2. SAMPLE ADAPTER

The flask containing the residual liquid was placed in a boiling-water bath, and to it were added 20 ml. of sodium hypochlorite solution, 5 grams of sodium chloride, and 10 grams of boric acid. Heating in the water bath was continued for 15 minutes, whereupon 20 ml. of sodium formate solution were added to destroy the excess hypochlorous acid. The contents of the flask were next boiled for 5 minutes, and cooled, and potassium iodide crystals, a few drops of ammonium molybdate solution, and 50 ml. of 2 *N* hydrochloric acid were added. The iodine liberated was titrated with standard sodium thiosulfate solution, starch being used as indicator. One milliliter of 0.1 *N* sodium thiosulfate is equivalent to 0.00158 gram of methyl bromide.

It has been determined that 2-liter air-sampling bulbs can be completely flushed out in 2 hours by a current of air flowing at the rate of 100 ml. per minute. This fact was established by placing a 2-liter bulb between the saponification apparatus and the sample adapter.



TABLE I. ACCURACY OF METHYL BROMIDE DETERMINATIONS BY THE METHOD DESCRIBED

MeBr Used Gram	Normality of $\text{Na}_2\text{S}_2\text{O}_3$	MeBr Found Gram	Error %
0.0480	0.1	0.0474	-1.2
0.0355 <sup>a</sup>	0.1	0.0352	-0.8
0.0333	0.1	0.0326	-2.1
0.0312	0.1	0.0304	-2.6
0.0299	0.1	0.0294	-1.7
0.0293 <sup>a</sup>	0.1	0.0286	-2.4
0.0288 <sup>a</sup>	0.1	0.0279	-3.1
0.0278	0.1	0.0271	-2.5
0.0244	0.1	0.0238	-2.5
0.0145	0.05	0.0140	-3.5
0.0125	0.1	0.0126	+0.8
0.0079	0.05	0.0077	-2.5
0.0065	0.05	0.0066	+1.5

Av. -1.7

<sup>a</sup> Run with 2-liter sampling bulb between sample and saponification apparatus.

The results are given in Table I. The average error of 13 analyses is -1.7 per cent; the greatest individual error is

-3.5 per cent. Samples ranged from 0.0480 to 0.0065 gram. The reproducibility and accuracy of these results are probably much greater than the reproducibility of fumigating conditions. The quantity of methyl bromide used in fumigating is usually about 2 pounds for each 1000 cubic feet of space, which is equivalent to approximately 0.064 gram in a 2-liter sample of air. Consequently the range of samples analyzed probably coincides roughly with that encountered in actual practice. The use of more dilute thiosulfate would permit the determination of smaller samples.

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## A Modification of the Markley Melting Point Apparatus

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THE Markley melting point apparatus (1) has been used satisfactorily for some time in this laboratory. The apparatus is essentially a large Thiele tube in which very rapid circulation of liquid is obtained through the use of an efficient stirrer, ensuring rapid interchange of heat between

the liquid, the melting point tube, and the thermometer. However, the usual methods of attaching the melting point tube to the thermometer have proved very troublesome. The use of a small rubber band or a small spring requires the removal of the thermometer from the bath, the attachment of the melting point tube, and the replacement of the thermometer in the bath each time that a reading is to be taken. Furthermore, there is always the danger of breaking the thermometer.

The apparatus was therefore modified by sealing to it two side arms of 3-mm. tubing in such a position and at such an angle that, when melting point tubes are inserted, their lower ends come in contact with the thermometer bulb. The side tubes should be long enough so that their open ends will come above the highest level to which the liquid in the apparatus will rise during its operation. It is advantageous to have the angle between the side tubes and the vertical as small as possible, about 35 degrees. Each side arm is wound with a short piece of wire (such as No. 25 chromel A), the end of which is bent over the opening in such a manner as to press the melting point tube against the inner surface of the side-arm tube. The melting point tube will thus be held steady and the lower end will be pressed in contact with the front of the thermometer bulb.

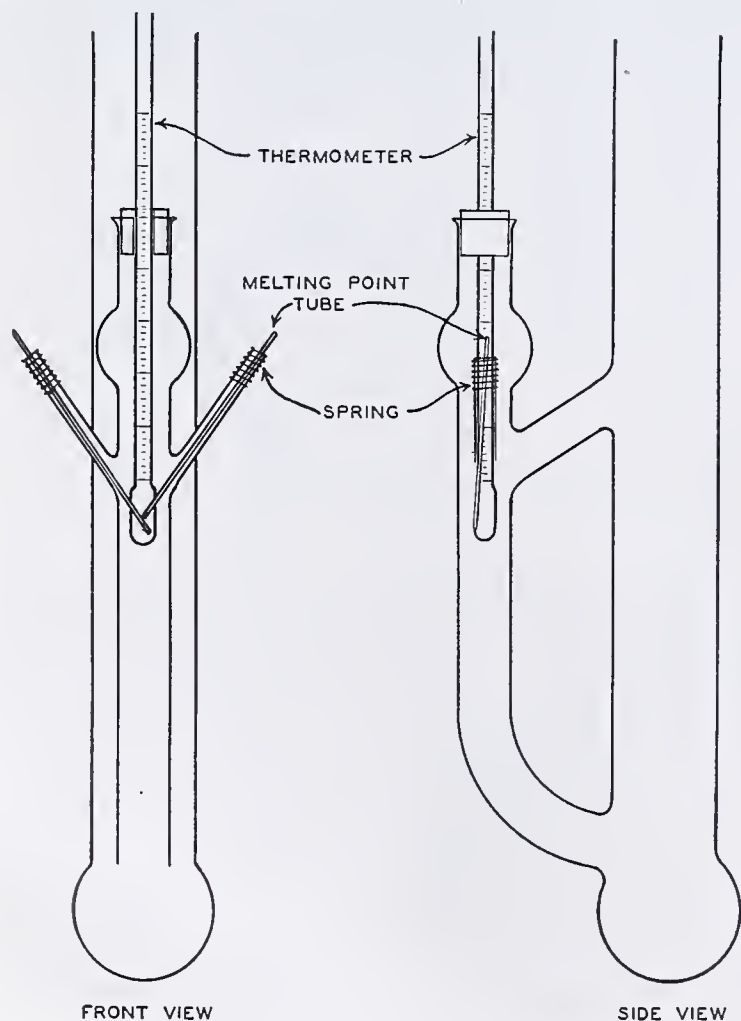
This modification of the apparatus simplifies the determination of melting points, since the melting point tubes can readily be inserted or withdrawn through the side arms. The thermometer may be left permanently in place by inserting it through a cork having a 90-degree sector cut out so that the cork will not block part of the thermometer scale.

A commercial grade of chlorinated diphenyl, as recommended by Dr. Markley in a private communication, has been found to be a satisfactory substitute for the usual sulfuric acid-potassium sulfate mixture.

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RECEIVED April 26, 1938.





# Gravimetric Determination of Zinc

## By the Mercuric Thiocyanate Method

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IN PLANNING some solubility measurements requiring the precise determination of zinc, a test was made of the gravimetric mercuric thiocyanate method studied by Cohn (3), Lundell and Bee (6), and Jamieson (4). The method has been used by Metler and Vosburgh (7) and Clayton and Vosburgh (2) and is one of the methods given for the determination of zinc in aluminum by Churchill and Bridges (1). The experiments indicated that, while the method had some definite advantages, a further study of some of the sources of error was desirable.

### Washing the Precipitate

Because of the appreciable solubility of zinc mercuric thiocyanate (5), Lundell and Bee (6) and Jamieson (4) washed the precipitate with a 0.002 molar solution of potassium mercuric thiocyanate and Metler and Vosburgh (7) washed twice with a 0.01 molar solution and twice with a 0.001 molar solution. Churchill and Bridges recommend a 0.001 molar solution.

Estimation based on the water remaining in a Gooch crucible after an ordinary washing with 0.001 molar wash solution gives 0.2 to 0.25 mg. for the amount of nonvolatile material remaining in the crucible. This estimate was confirmed by experience.

Experiments on the change in weight of a zinc mercuric thiocyanate precipitate on washing showed that washing with a 0.001 molar wash solution at a temperature of 5° to 10° C. caused negligible change. Preliminary washing with a more concentrated solution was undesirable, as it often resulted in the retention of significant quantities of the reagent. A 0.001 molar solution at 20° to 30° C. caused an appreciable loss of precipitate.

**WASHING PROCEDURE.** In the preparation of the Gooch crucibles the final washing before drying and weighing was made with 0.001 molar wash solution. Before a filtration was begun, the crucible was well rinsed with water or the wash solution. The mother liquor was then decanted through the crucible and the precipitate washed at least twice by decantation with cold (5° to 10° C.) 0.001 molar wash solution. Then the precipitate was transferred to the crucible and washed at least twice.

Erratic results could often be explained as the result of inefficient washing. It is believed that the procedure just given will lead to satisfactory washing if followed exactly.

### Method of Precipitation

The size of the crystals varies considerably with the method of precipitation. When the reagent is added rapidly, some of the crystals are too small. A slow rate of addition results in supersaturation followed by a sudden precipitation of small crystals. However, if crystallization is induced by rubbing the sides of the beaker or by seeding, the crystals are large enough to be handled conveniently and do not creep or stick to the beaker or stirring rod.

The following was found to be a convenient method of obtaining crystals of the right size and was used in all the experiments described below:

Three small drops of the solution containing the sample were transferred on the end of a stirring rod to a small test tube or vial and a drop or two of a 0.1 molar solution of the reagent was added. The solution was stirred and the glass rubbed to induce

crystallization and then the mixture was transferred quantitatively to the main body of the solution. If a visible turbidity did not result, the process was repeated. The reagent was then added in small drops at a rate of about 2.5 ml. per minute with mechanical stirring.

### Procedure

The procedure used in the study of other conditions was as follows:

A solution was prepared by dissolving a weighed portion, about 1 gram, of spectroscopically pure zinc, obtained through the courtesy of the Research Division of the New Jersey Zinc Company, by means of 8 or 9 ml. of 8 molar nitric acid solution, making up to about 200 ml., and weighing the solution. For analysis, weighed portions, usually about 10 grams each, were taken. The sample was diluted to about 100 ml. Enough nitric acid was present with the sample to make the acid concentration after dilution about 0.1 molar. In a few cases sulfuric acid was used, and in some of the experiments additional sulfuric or nitric acid was added. The solution was next seeded and the precipitation carried out as described above.

A 0.1 molar solution of the reagent, the preparation of which is discussed below, was used. The solution was 0.01 to 0.02 molar with respect to excess reagent after precipitation; for 0.03 gram of zinc, either 15 or 30 ml. of 0.1 molar solution of the reagent were added, and 45 ml. were shown to be not too much. The precipitate was allowed to digest under the mother liquor at room temperature for at least 1 hour. A Gooch crucible was rinsed with water (or wash solution) and the mother liquor decanted through it. The precipitate was washed at least twice by decantation with cold 0.001 molar wash solution, transferred to the crucible, washed twice in the crucible, and finally dried at 105° to 110° C. and weighed.

### Composition of the Reagent

It was found best to prepare the reagent with excess of thiocyanate. When 10 per cent excess of mercuric chloride was present, the results of two determinations were 8 parts in 1000 too high. When the reagent was made of equivalent quantities of the two compounds, five determinations gave an average of 2.4 parts in 1000 too high. When thiocyanate was present in excess, however, the results were practically correct. The reagent was usually made with a 10 per cent excess of thiocyanate, but 17 per cent excess gave equally good results.

The reagent may also be made from mercuric thiocyanate. One sample of commercial mercuric thiocyanate was found

TABLE I. DETERMINATION OF ZINC IN KNOWN SAMPLES

(The quantity of zinc present was from 0.037 to 0.046 gram, the weight of the precipitate varying from 0.28 to 0.35 gram)

No. of Detns.	Additions Grams	Error (Observed - Calculated)		
		Maximum	Algebraic mean Parts in 1000	Arithmetic mean
47	None	+3.4	+0.3	±1.2
4	1.8 H <sub>2</sub> SO <sub>4</sub>	2	0.5	1
2	5 H <sub>2</sub> SO <sub>4</sub>	1	1	1
2	9 H <sub>2</sub> SO <sub>4</sub>	5	5	5
2	1.3 HNO <sub>3</sub>	2	0.1	2
2	2.6 HNO <sub>3</sub>	0.3	0.3	0.3
4	3.9 HNO <sub>3</sub>	-5	-4	4
2	2 (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-1	-1	1
2	3 (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	+9	+5	5
2	1.5 NH <sub>4</sub> NO <sub>3</sub>	+5	5	5
2	1 KCl	+5	2	3



unsatisfactory, impurities which were present probably being responsible for the erratic results obtained.

### Results

Table I gives the results of a number of analyses made as described. To some of the samples various additions were made as shown. While the results of analyses that failed because of improper control of conditions are not included, it is believed that the data in the table are representative. The method is capable of giving very good results when no interfering substances are present. The algebraic mean of the errors is 0.3 part in a thousand, indicating slightly high results. The average error without regard to sign was 1.2 parts in a thousand. Sulfuric acid up to 5 grams and nitric acid up to 2.5 grams may be present, but larger quantities lead to high results. The quantities of salts permissible are less.

Results obtained with samples containing 0.02 and 0.09 gram of zinc were as satisfactory as the results with 0.04 to 0.05 gram.

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## Moisture Determination

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OF INTEREST to those who use the Dean-Stark method of moisture determination will be this simple supplementary apparatus. It assists in reading the volume of aqueous distillate and entirely eliminates the error due to parallax which is so prevalent in this determination.

The experienced operator will appreciate the difficulty of obtaining an accurate reading by attempting to hold the trap level and taking a reading with the naked eye. In instances where the material to be tested is of high moisture content and only a 10-gram sample can be used, an error of 0.1 cc. in reading the meniscus will mean an error of 1.0 per cent in the ultimate result. The error in larger samples will of course be proportionately less, but it is difficult if not impossible to eliminate such an error without some kind of an aid to hold the trap in its intended position while reading, and something to aid the eye and keep the eye and meniscus in the same plane.

The author has found the supplementary apparatus particularly valuable where the Dean-Stark method of

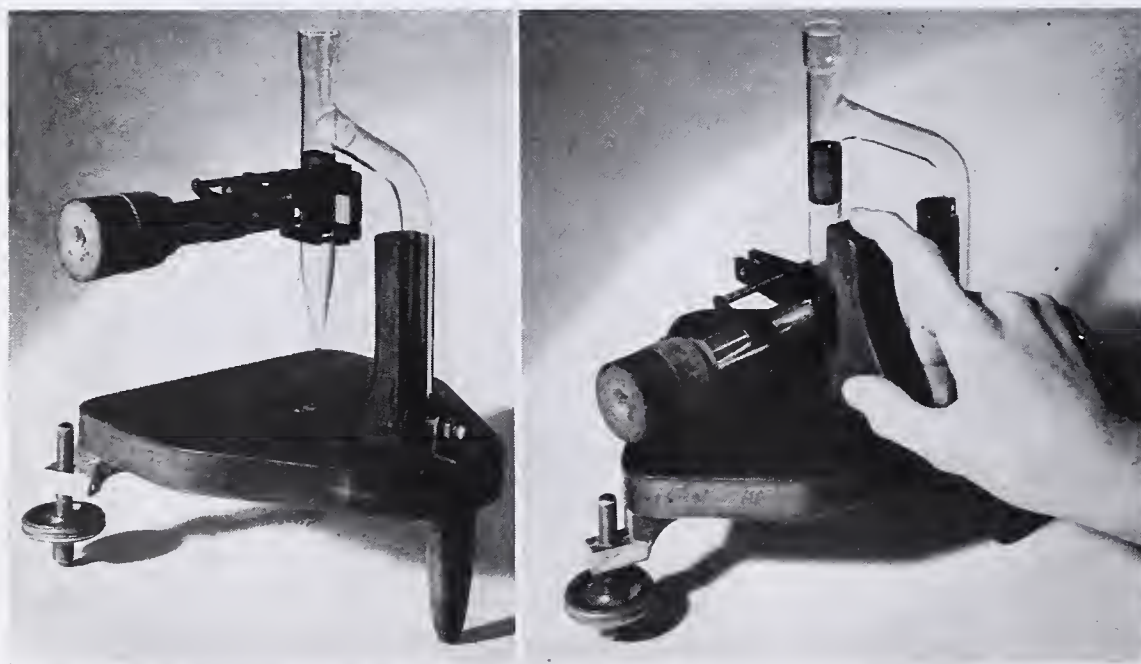
moisture determination has been adapted to high-moisture compounds.

The base of the apparatus stands upon three legs. Two of these are of the adjusting-screw type, and are used in conjunction with the bubble level to facilitate the leveling of the base. From the base arises a support for holding the trap perpendicular. A small spring clamp at the bottom holds the trap rigid.

The eyepiece is an ordinary meniscus reader (Arthur H. Thomas Co. 2501) to which is added a wooden spool, one end of which is beveled to rest snugly in the eyepiece and is tightly held by a short piece of Gooch rubber tubing. Through the exact center of the spool, which is about 35 mm. long and 30 to 35 mm. in diameter, a 3-mm. hole is bored.

It is advisable to add to the top layer of distillate a few cubic centimeters of a solution of an oil-soluble dye. This will color only the top layer, further distinguishing the two layers of liquid. In practice it is best to place the eyepiece below the junction of the liquid and raise it till the entire upper layer appears colored (by the oil-soluble dye).

If the junction of the liquids should come at the tapered part of the trap, the jaws of the eyepiece will obviously not hold it in a horizontal position. This difficulty is overcome by using a block of wood 90 × 55 × 24 mm., holding the 55-mm. end flat against the base with the 90-mm. end against the graduated portion of the trap. The part of the clamp outside the V-shaped jaws may be clamped against the block and the eyepiece raised or lowered until the proper level is reached.



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# Reduction of Selenious Acid by Thiocyanic Acid

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RECENTLY Ljung (20) proposed a new qualitative test for selenium. Ammonium thiocyanate is added to the boiling solution which is about 6 *N* in hydrochloric acid, to precipitate any selenium present as selenious acid, and it is claimed that one part of selenium can be detected in 20,000,000 parts of solution. The statement is made that there "is an exact stoichiometric relationship between the reacting ions" but it is admitted that the equation given



does not represent the correct ratio between the weights of thiocyanate and selenite that take part in the reaction.

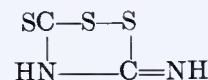
(1) The equation does not balance; the sum of the electron charges on the left is +2 and on the right is -6 which means that eight electrons have been created, whereas in a properly balanced ionic equation the sum of the charges on the right must equal the sum of the charges on the left. (2) The reaction represents a reduction of quadrivalent selenium to the neutral state. If the thiocyanate ion accomplishes this reduction it must itself undergo oxidation; a reduction can never take place without an equivalent oxidation. The formation of  $\text{CN}^-$  and  $\text{S}^{--}$  from  $\text{CNS}^-$  cannot be regarded as representing an oxidation. (3) Since the reaction takes place in the presence of a large excess of hydrochloric acid, it is impossible that an appreciable quantity of either  $\text{CN}^-$  or  $\text{S}^{--}$  can be formed, for in acid solutions these ions will unite with  $\text{H}^+$  to form undissociated hydrocyanic acid and hydrogen sulfide.

A study of the literature shows that Ivanov (10) used thiocyanate for the quantitative precipitation of selenium from acid solutions. He mixed together fairly strong solutions of selenious acid and ammonium thiocyanate and then, upon the addition of considerable hydrochloric acid, a yellow compound was precipitated which proved to be  $(\text{HCNS})_2 \cdot \text{H}_2\text{SeO}_3$ . The compound was fairly stable in the cold and Ivanov was able to establish its constitution by analysis. He was unable to prepare a similar compound with tellurium and thought that the reaction might be used to separate selenium from tellurium. As decomposition took place in hot solutions, Ivanov diluted the solution, heated it for 12 hours on the water bath, and allowed it to stand overnight. Under these conditions, he was able to accomplish complete precipitation of all selenium (0.1 to 0.4 gram) but the precipitates were always contaminated with sulfur.

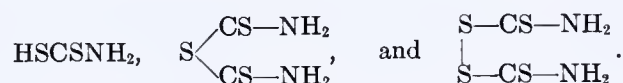
Ivanov's conditions were very different from those recommended by Ljung. Ljung boiled his solutions only a few minutes, at a slightly higher temperature than Ivanov. Ivanov did not attempt to write an equation to represent this decomposition. It is difficult to do this because thiocyanic acid itself, in the presence of hot hydrochloric acid, is very unstable.

The instability of thiocyanic acid has been known for a long time. Wöhler (38) was probably the first to attempt to prepare pure thiocyanic acid and to recognize its instability. Some of its decomposition products were studied in the laboratory of Wöhler's friend, Liebig (19). Since then the literature on thiocyanic acid and related compounds has become very voluminous, but excellent papers have been written by Völckel (36), Klason (14), and Stokes and Cain (32).

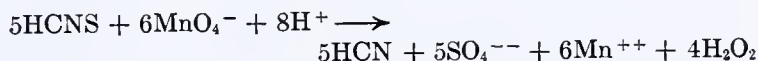
Wöhler (38) found that thiocyanic acid is a colorless liquid at ordinary temperatures but decomposes on standing, with the formation of a yellow substance which is now recognized as isoperthionic acid,  $\text{H}_2\text{C}_2\text{N}_2\text{S}_3$ , and given the following structure:



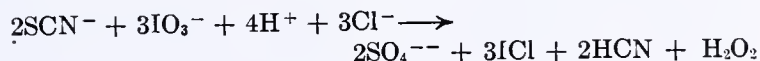
According to statements in the literature (14, 36) the following substances are also likely to result from the decomposition of thiocyanic acid: hydrocyanic acid, formic acid, carbon dioxide, carbonyl sulfide, carbon disulfide, hydrogen sulfide, and ammonium salts. The action of mineral acid on a thiocyanate is also likely to cause the formation of



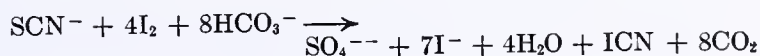
The behavior of thiocyanic acid toward oxidizing agents has been the subject of numerous papers and many quantitative methods of analysis have been based on the formation of thiocyanates and subsequent oxidation of the thiocyanic acid. Thus, potassium permanganate in acid solutions oxidizes thiocyanic acid to sulfuric and hydrocyanic acids. This reaction appears to have been discovered by Erlenmeyer (5) but other chemists have studied it (1, 4, 6, 7, 9, 12, 21, 22, 25, 26, 27, 31, 37). The reaction can be expressed by the equation



A similar oxidation of thiocyanic acid is the basis of many iodometric methods. Here also the oxidation of thiocyanic acid results in the formation of sulfuric acid from its sulfur and either hydrocyanic acid or a product such as cyanogen iodide from its nitrogen. Thus with potassium iodate in the presence of hydrochloric acid, Jamieson, Levy, and Wells (11) found the reaction to be



but Rupp and Schied (29) under different conditions accomplished the oxidation with iodine according to the equation



Similar oxidations have been carried out with bromine, potassium bromate, hypobromite, hypochlorite, and chromic acid (2, 3, 6, 8, 13, 15, 16, 17, 23, 24, 28, 30, 33, 34, 35).

This by no means exhausts the literature on the oxidation of thiocyanate in methods used in quantitative analysis. During the last thirty years, for example, at least twenty-five papers have been published on the thiocyanate content of saliva, urine, blood, and other biological fluids. Some were published in journals which are not easily accessible and abstractors often forgot to mention how the analyses were made, but enough were examined to show that in practically every case the sulfur atom of the thiocyanate anion is oxidized to sulfate and in most cases the nitrogen is left as hydrocyanic acid; in some cases the determination is based upon the argentometric titration of the hydrocyanic acid formed.

Under other conditions the oxidation of thiocyanic acid does not take place quantitatively in any one direction and the literature describes products called Schwefelcyan, Persulfocyan, Pseudoschwefelcyan, Kanarin, Überschwefelblausäure, Persulfocyanensäure, Dithiocyanensäure, Dithiocarbaminsulfid, and Melanin which have been obtained directly or indirectly by the oxidation of thiocyanic acid. In some cases,



the same substance has been described under different names, and the study of these papers is complicated by the fact that in many papers written in the nineteenth century, the atomic weights and equivalents were different from those recognized today. As long ago as 1846, the complaint was made that the literature on the decomposition products of thiocyanic acid was confusing and later workers have not been able to duplicate some of the results (18).

During the last six months, several sophomore students in this laboratory have experimented with small quantities of thiocyanic acid and selenious acid in the presence of considerable hydrochloric acid. As in the experiments described by Ljung (20), the solutions were boiled for a short time after the addition of the thiocyanate. The deposited selenium was weighed in nearly every case and futile attempts were made to establish definite relations between the quantities of selenium deposited and of some decomposition product formed. From these experiments some interesting conclusions can be drawn.

1. When potassium thiocyanate is added to boiling 6 *N* hydrochloric acid containing no selenious acid, decomposition of the thiocyanic acid, formed by the action of hydrochloric acid on the alkali salt, takes place promptly and the principal products appear to be  $\text{NH}_4^+$ , hydrogen sulfide, and carbon dioxide. The decomposition can be expressed fairly well by the equation



In opinion formed before reading the literature, the reaction is not as simple as this equation would indicate. Wöhler and Liebig knew this a century or so ago. The author and his associates have never been able to get approximately one molecule of ammonium salt, one of carbon dioxide, and one of hydrogen sulfide from the decomposition of one molecule of potassium thiocyanate, although in every case they have found these three products. They have been unable to get tests for any appreciable quantity of hydrocyanic acid either by the odor of the distillate or by special tests for hydrocyanic acid, including the argentometric test which has been used for determining the small quantity of thiocyanic acid in saliva on the basis of the hydrocyanic acid formed by treatment with an oxidizer.

2. The reaction between thiocyanic acid and selenious acid varies, as stated by Ljung, at different concentrations of hydrochloric acid and at different temperatures. When the thiocyanate and selenious acid solutions are mixed, the first thing noticed is a yellow color, which may be due to the formation of isoperthionic acid (19, 38) or to the yellow complex studied by Ivanov (10). At the boiling temperature, selenium soon begins to precipitate and the reaction is capable of detecting the presence of very small quantities of selenium, but cannot be recommended for the determination of this element. The equation



shows how the reaction can take place. In two experiments Robert N. Bonnett obtained 2 Se to 1  $\text{SO}_4^{--}$ , but in other experiments he obtained quite different results. S. V. Arnold obtained 1.43 Se to 1  $\text{SO}_4^{--}$ , and Max Cohen 1.57 Se to 1  $\text{SO}_4^{--}$ . Bonnett observed that when the concentration of the hydrochloric acid was changed from 6 *N* to 8 *N* only 65 per cent as much  $\text{SO}_4^{--}$  was formed and some of his precipitates were proved by both physical and chemical examination to contain sulfur. Corroborative experiments were carried out by others, especially W. P. Lamb and R. D. Haworth, Jr. Working under different conditions, Ivanov (10) found that sulfur was always precipitated with the selenium.

It is possible to conceive the  $\text{CNS}^-$  anion as containing carbon with a valence of +4, nitrogen with a valence of -3,

and sulfur with a valence of -2. The experiments of the author and his associates show that the principal products of the decomposition of thiocyanic acid are carbon dioxide, in which carbon has a valence of +4,  $\text{NH}_4^+$  in which nitrogen has a valence of -3, and hydrogen sulfide in which sulfur has a valence of -2. In other words, the spontaneous decomposition of thiocyanic acid from a boiling solution which is 6 *N* in hydrochloric acid results for the most part in a reaction which is neither an oxidation nor a reduction, because the sum of the valences of carbon, nitrogen, and sulfur is the same in the products as in the original compound. In the presence of selenious acid, the principal product of the oxidation appears to be sulfuric acid in which the sulfur atom has the valence +6, so that the oxidation is really due to the sulfur atom and a part of the sulfur is sometimes oxidized only to the neutral state. Hydrogen sulfide, which is a product of the spontaneous decomposition of thiocyanic acid, reacts with selenious acid as follows:



For quantitative purposes, the reduction of selenious acid by potassium thiocyanate and hydrochloric acid is not satisfactory because it is practically impossible to make the reduction take place in accordance with a single definite equation.

The fact that the ammonium ion, but rarely if ever the hydrocyanic acid molecule, is formed when selenious acid is reduced by alkali thiocyanate is of particular interest, but is not surprising because selenium or selenious acid has found extensive use as a catalyst in the Kjeldahl digestion, when it is desired to convert the nitrogen of an organic compound into ammonium salt.

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# A Balanced Circuit for Electrometric Titration

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RESCORLA, Carnahan, and Fenske (4) have included in their valuable study of solvents for the electrometric titration of petroleum oils a titrimeter circuit which has some points of advantage over the bridge-type circuits of Garman and Droz (2) and Willard and Hager (5). However, this circuit is so expensive as to discourage its use unless most of the parts required happen to be on hand. The circuit shown in Figure 1 was designed to avoid unnecessary expense and to simplify construction. The cost of parts for this circuit is less than one-third that of Rescorla, Carnahan, and Fenske, and the space required is reduced in about the same proportion, yet the stability is as great, even though the sensitivity is increased by the use of an output tube of higher amplification.

The stability of the circuit against changes in line voltage is due in part to the use of two opposed tubes, but since the pentode has a much greater amplification than the triode, the circuit is balanced by drawing part of the grid bias of the pentode from the bleeder circuit. Therefore,  $R_1$  should be carefully adjusted until line-voltage changes produce a minimum effect on the meter reading. Adjustment will be most convenient if  $R_1$  consists of a 150-ohm fixed resistor and a 100-ohm wire-wound volume control, but this is necessary so seldom that a simple wire-wound

resistor with an adjustable clip may be used. After this adjustment, momentary fluctuations of line voltage should have no effect upon the meter tested with potentiometer  $R_5$  set to give a reading of any magnitude on the meter scale. However, prolonged deviations of voltage will cause a drift of the reading due to change of cathode temperature. With modern control of commercial line voltage, it is unusual to find conditions where voltage will fluctuate sufficiently to interfere with even the more sensitive electrometric titrations; but if voltage changes are large and prolonged, the bridge circuit of Garman and Droz (2) will probably be more satisfactory, unless a voltage control is used.

The power transformer,  $T$ , may be one designed for midget radio use and, if it is skimmed in iron to save weight and size, the increased magnetic saturation will reduce voltage fluctuations in the output. Since there is only a difference of about 85 volts in potential between the cathodes of the two tubes, they may use the same filament winding. If two filament windings are present, they should be used, with each cathode connected to the center tap of its own winding.

The milliammeter connection shown allows about a half milli-ampere plate current to flow at zero reading, so that the entire scale of the instrument may be used. If the simpler connection as shown by Rescorla, Carnahan, and Fenske is desired,  $R_7$  is omitted and  $R_4$  and  $R_5$  are combined to form a single 5000-ohm resistor, but scale readings below about 0.1 milliamperes will deviate considerably from linearity.

The milliammeter chosen should have a fairly long scale, pref-

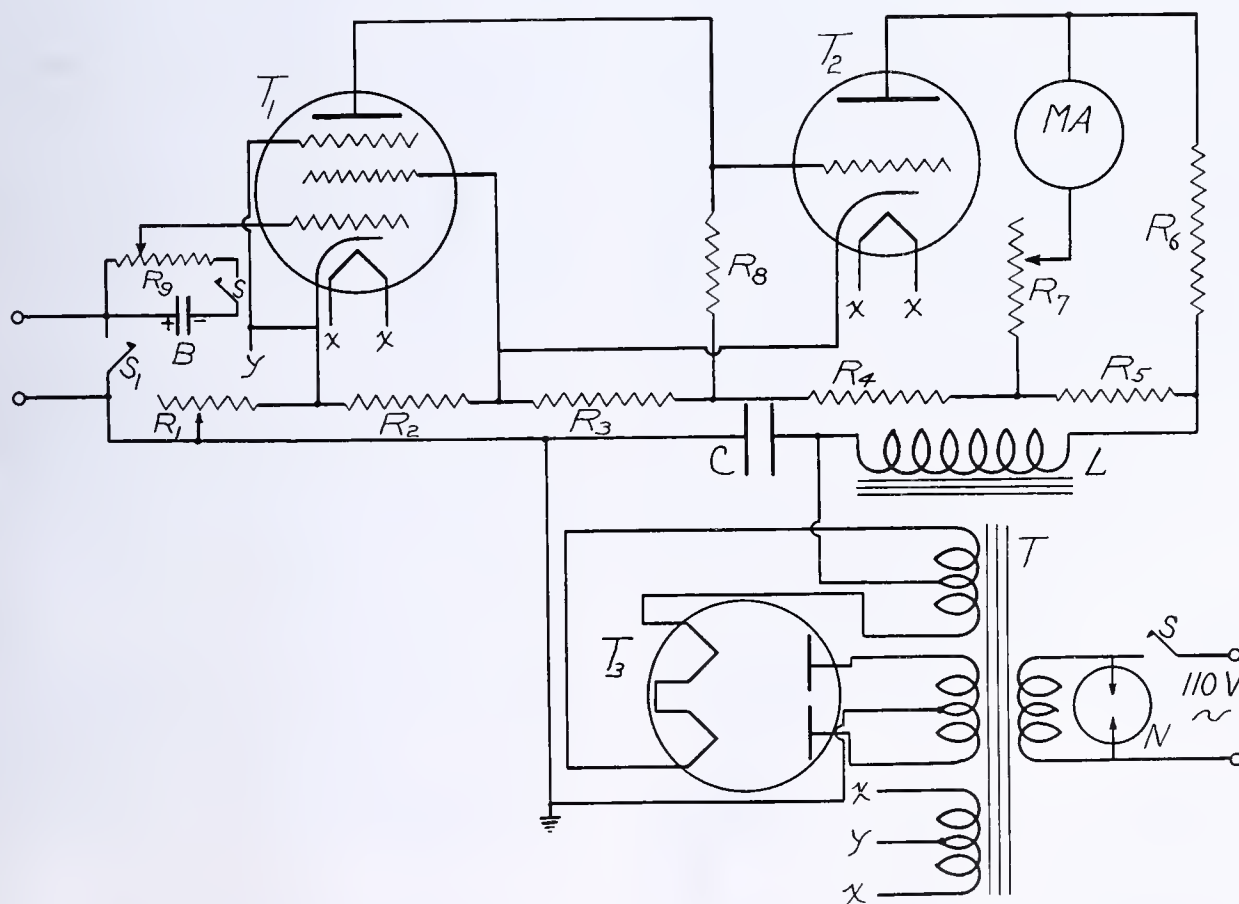


FIGURE 1. CIRCUIT

B.	Battery, 1.5 or 3 volts
C.	Electrolytic condenser, 8 mfd.
L.	Choke, 30 henries, not over 200 ohm direct current resistance
MA.	Milliammeter, 0 to 1 milliamperes
N.	Neon pilot bulb, 0.25-watt, candelabra base
R1.	250-ohm adjustable resistor
R2.	5000 ohms, 5 watts
R3.	10,000 ohms, 10 watts
R4.	3500 ohms, 5 watts
R5.	1500 ohms, 5 watts
R6.	50,000 ohms

R7.	100,000-ohm potentiometer or adjustable resistor
R8.	500,000 ohms
R9.	10,000-ohm wire-wound potentiometer
S, S1.	Double-pole single-throw switch
S2.	Single-pole single-throw switch
T.	Power transformer, delivering 350 volts each side of center tap
T1.	Type 6C6 or 57 tube, according to filament voltage available
T2.	Type 76 or 56 tube, according to filament voltage available
T3.	Type 80 or similar rectifier tube



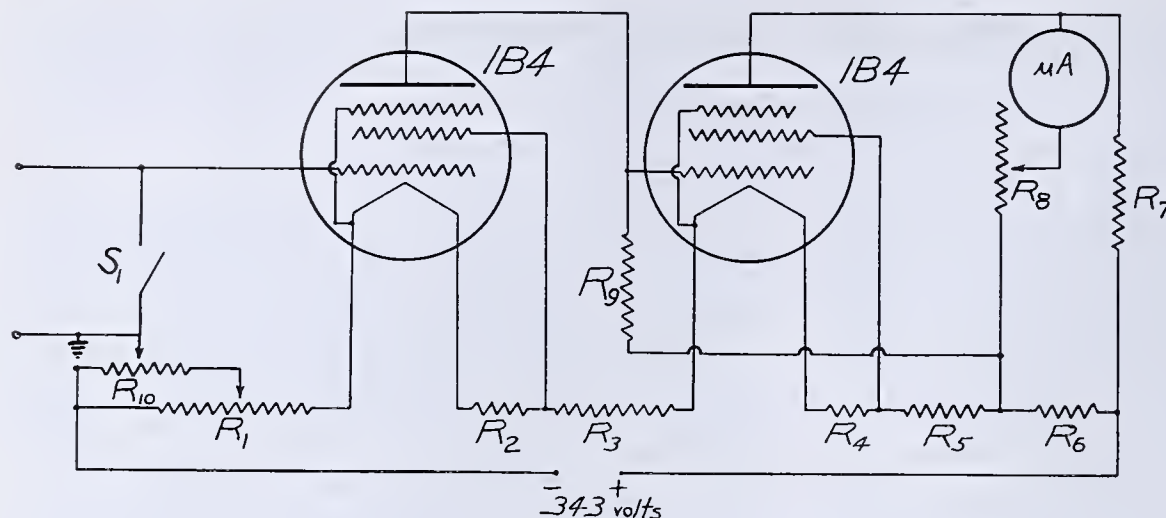


FIGURE 2. CIRCUIT

$\mu A$ .	Microammeter, full-scale 200 microamperes or less
$R_1$ .	100-ohm resistor with adjustable tap
$R_2$ .	1100 ohms, 10 watts
$R_3$ .	500 ohms, 10 watts
$R_4$ .	1100 ohms, 10 watts
$R_5$ .	1100 ohms, 10 watts
$R_6$ .	1750 ohms, 20 watts
$R_7$ .	500,000 ohms
$R_8$ .	500,000 ohms
$R_9$ .	500,000 ohms
$R_{10}$ .	10,000-ohm wire-wound potentiometer
$S_1$ .	Switch

erably over 3 inches, but high accuracy in calibration is not essential. Suitable meters can be purchased for \$4.50 and up.

Sensitivity is adjusted by changing  $R_7$ , which may be either a radio volume control or a resistor tapped at several points. A fixed resistor may be used if it is large enough to protect the meter from damage and no change in sensitivity is desired. With  $R_7$  at the full 100,000 ohms, about 0.6-volt change in voltage of the input is required to give a full-scale deflection of the meter, while if only 10,000 ohms are used, only about 0.1 volt is required. Higher sensitivity is available by using a microammeter instead of the milliammeter, but this is hardly feasible unless a good voltage control is used.

Voltage control may be desired either because of excessive fluctuations in line voltage, or when high sensitivity and reproducibility of measurements are necessary. Constant-voltage transformers are available, and will give excellent results when connected to keep the primary of the power transformer,  $T$ , at constant voltage. The regulation of an electronic voltage control is still more accurate, and this can be constructed at considerably less cash outlay for parts, though it may cost more if time of assembly is charged against it. Description of such a control is to follow in another paper.

However, the application of direct current from the electronic control to the circuit in Figure 1 is not a great improvement unless the tube filaments can also be supplied with constant voltage, as from a storage battery. To avoid this difficulty, the circuit shown in Figure 2 was designed to operate entirely from a direct current voltage regulator of reasonable capacity. The voltage across the bleeder is specified as 343 volts, and if this is exceeded the life of the tubes will be considerably shortened. If an accurate voltmeter of this range is not available, it will be equally satisfactory to adjust the voltage source until the voltage drop across each of the tube filaments is 2 volts, or to a total current of 60 milliamperes, if either of these can be measured with fairly high accuracy.

This circuit as shown gives about the maximum sensitivity conveniently available. If less sensitivity is required, a 0- to 1-milliammeter and a type 30 tube may be used in the output, with a saving of several dollars. In this case,  $R_7$  may be 50,000 ohms and  $R_8$ , 100,000 ohms.

Either arrangement is suitable for measurements of potential from hydrogen or quinhydrone electrodes, from thermocouples, and the like, and will retain its calibration over considerable periods. Preparation should be made for convenient checking of calibration, as with buffer solutions for pH measurements, or with a potentiometer for millivolt readings.

For reading pH values between 3 and 8 with the quinhydrone electrode, it is often convenient to reverse the usual connections, connecting the saturated calomel electrode to the ground connection and the quinhydrone electrode to the negative or grid lead. The method of calibration is illustrated by the following example, in which the materials to be studied are all expected to lie between

4.0 and 6.0 pH. Buffer solutions of these maximum and minimum values are made up by the method of Clark (1). The quinhydrone electrode is placed in the 4.0 pH buffer and the bias potentiometer  $R_{10}$  adjusted to give a zero meter reading. The final adjustment may be made with the maximum sensitivity or zero setting of  $R_8$ .  $R_8$  is then increased to lower the sensitivity, and adjusted to give exactly a full-scale reading after the quinhydrone electrode has been changed to the 6.0 pH buffer.

The linearity of response is well within the accuracy to be expected in the preparation of such buffer solutions, as is shown by the data recorded in Table I which were read to the nearest 2 microamperes using this circuit with a 0- to 200-microampere meter. The buffer solutions were checked to the nearest 0.5

millivolt by means of a potentiometer. To test the stability of the instrument, the readings were repeated on the two following days with no change in the adjustment of the titrimeter or of the electronic voltage control. However, this stability is not to be relied upon unduly, and a daily or even more frequent check of calibration is to be recommended.

TABLE I. READINGS OF TITRIMETER WITH QUINHYDRONE ELECTRODE IN STANDARD BUFFER SOLUTIONS

Nominal pH	4.0	4.8	5.4	6.0
E. m. f., millivolts	218.0	171.5	134.5	99.0
Meter reading, microamperes:				
First day	0	78	140	200
Second day	0	80	142	202
Third day	-2	76	138	198

It is possible to use this instrument, or similar ones, with the glass electrode by checking against buffer solutions of the correct pH so as to balance out the voltage drop and polarization, but this is rather a slovenly makeshift. It is much better to introduce a condenser for ballistic discharge as in the method of Hemingway (3), and when this is done an alternating current amplifier as shown by him is preferable to direct current amplification.

No grid resistor is shown on the input tube in either Figure 1 or Figure 2. None is necessary unless there is danger of considerable positive voltage being applied to the grid accidentally, in which case 100,000 ohms may be introduced. With good shielding, resistance up to 10 megohms may ordinarily be used, but there will be a noticeable decrease in sensitivity with values above 1 megohm.

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# A Simplified Precision Oil Manometer

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IN A PREVIOUS paper (1) the advantages of oil manometers for precision measurement of pressure, particularly in the range of 40 mm. or less, were pointed out. An oil gage was there described which was, in effect, a double U-tube type manometer, in which both oil and mercury are employed, the mercury serving, however, as a mobile "backing" medium for the oil column and not for pressure measurement.

The oil manometer described in the present paper is much simpler in construction, and is, in effect, a single U-tube requiring no second backing liquid such as mercury to render possible movement of the oil column from the closed end. A grease-sealed, well-ground stopcock constitutes the closure mechanism, comparable to the closed end of an ordinary U-tube. The dislodging of the oil is accomplished by a slight rotating movement of the plug of this stopcock. When

opened, the stopcock permits communication with the pumping system. A large expansion chamber just below this stopcock, as in the case of the earlier mercury-oil gage (1), serves to reduce to a negligible value the effect of any residual trace of gas in the closed end. The lower chamber serves for degassing and "conditioning" of the manometric liquid, as explained below.

## Preparation of Manometer for Use

A quantity of purified oil, ester, or other nonvolatile liquid, sufficient to fill reservoirs *f* and *g* and still leave several cubic centimeters of liquid in bulb *h*, is introduced through *a* before the fine capillary and rubber tube, *b*, is attached. Tube *b* is slipped on *a*, stopcock *P* is locked, stopcocks *d* and *e* are opened, and a good vacuum pump is connected at *c* and run continuously during the conditioning of the manometer. After rapid degassing has ceased at room temperature, the liquid in reservoir *h* is gently heated until the volatile material has been driven off. In order to remove any volatile material which may have collected in *k* and *f*, the hot oil is manipulated a couple of times between reservoirs *h* and *f*. After the oil has cooled somewhat, it is forced from reservoir *h* to a level slightly above stopcock *d* by closing stopcock *e*, and allowing air to leak very slowly into reservoir *h* through stopcock *P*. When the liquid passes through stopcock *d*, the plug is crossed in *d* and then in *P*. If the manometer has been thoroughly conditioned, the level of the oil will not fall when stopcock *e* is opened even at low pressure. A rotation of the plug of stopcock *d* through a few degrees will be necessary to dislodge the oil.

The pressure is read by measuring the difference in levels of the oil in *k* and *M*. Tube *k* and auxiliary tube *M* have the same inside diameter, so that errors due to capillarity will be eliminated. Tube *M* is constricted at *r* to temper undue or sudden movement of the oil through the tube.

At the end of each day of use, and while the manometer is still evacuated, stopcock *e* should be closed and air should be allowed to leak slowly into bulb *h*, forcing the level of the oil through reservoir *f*. Stopcock *d* should then be carefully opened, permitting a small amount of additional oil to pass through, which will carry with it any trace of gas that may have collected. None of the liquid already above the stopcock should be allowed to run into reservoir *f*, except when the oil is to be reheated for reconditioning. To preserve high accuracy of the gage, it should be reconditioned when the oil can be dislodged without rotating the plug of stopcock *d*. When not in use, the gage should be left with stopcocks *d*, *e*, and *P* crossed.

In Table I are shown comparative readings made on five manometers: two separate simplified precision oil manome-

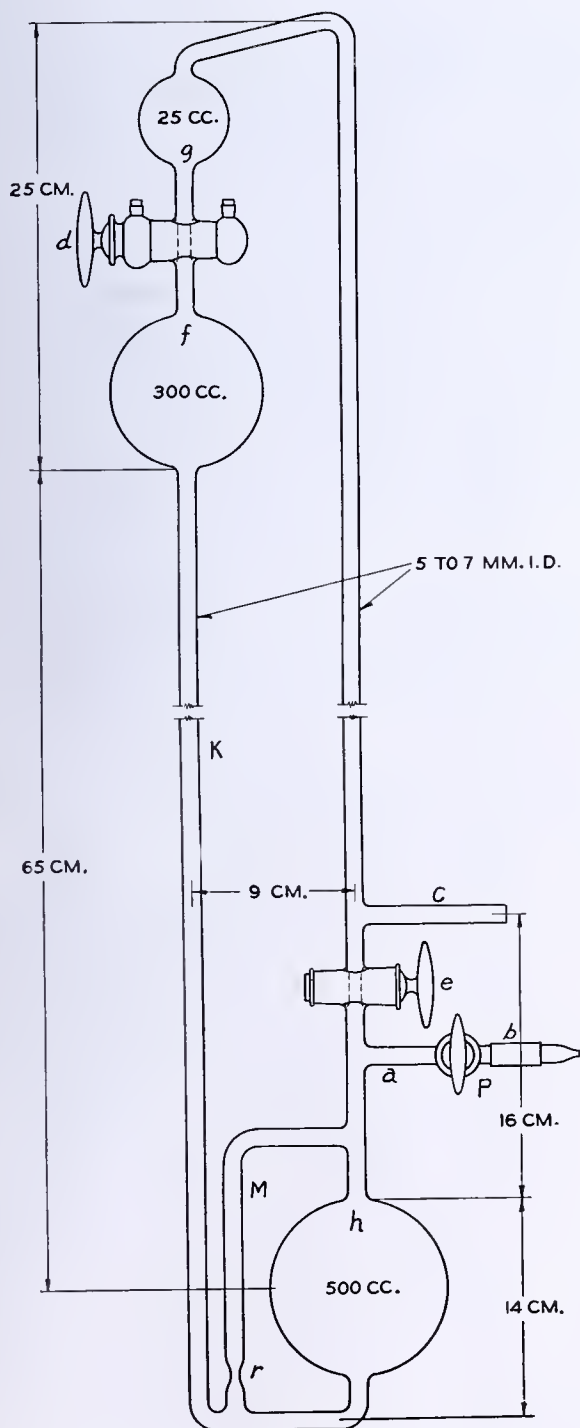


TABLE I. COMPARATIVE READINGS AT ROOM TEMPERATURE (26° C.)

Simplified Oil Gages				Previous Mercury-Oil Gage <sup>a</sup>		Zimmerli Gage	U-manometer
Apiezone-A		Light mineral oil		Apiezone-B			
Mm. Oil	Mm. Hg <sup>b</sup>	Mm. Oil	Mm. Hg <sup>b</sup>	Mm. Oil	Mm. Hg <sup>b</sup>	Mm. Hg	Mm. Hg
11	0.71	11	0.70	11	0.71	0.7	0.7
14	0.90	14	0.89	14.5	0.93	0.9	1.0
33	2.12	34	2.15	33	2.12	2.1	2.0
52	3.34	53	3.35	52	3.34	3.4	3.2
69	4.42	70	4.43	69	4.42	4.4	4.6
88	5.64	90	5.70	88	5.64	5.7	5.7
98	6.28	100	6.33	98	6.28	6.3	6.0
111	7.11	113	7.15	111	7.11	7.1	7.4
128	8.2	130	8.2	128	8.2	8.2	8.5
142	9.1	145	9.2	142	9.1	9.1	9.3
162	10.4	165	10.4	162	10.4	10.4	10.3
202	12.9	205	13.0	202	12.9	13.0	13.2
257	16.5	260	16.5	256	16.4	16.5	16.1
350	22.4	356	22.5	351	22.5	22.5	22.7
470	30.1	478	30.2	470	30.1	30.2	30.4
598	38.3	608	38.4	598	38.3	38.4	38.5
39	2.50	40	2.53	39	2.50	2.5	2.3

<sup>a</sup> The mercury-oil gage was provided with an auxiliary tube similar to that used in the oil gages.

<sup>b</sup> Calculated.



ters, one containing Apiezone-A,<sup>1</sup> and the second light mineral oil (white paraffin oil, U. S. P., Eimer and Amend Co., New York, N. Y.); the mercury-oil manometer previously described (1), using Apiezone-B;<sup>1</sup> a Zimmerli vacuum gage (3); and a well-made, simple U-type mercury manometer. In order to ensure constant pressure during each set of observations, a pressure-control unit (2) was used in the system with the communicating tube placed at a point equidistant from all the gages.

Readings on the Zimmerli gage had to be made with considerable care, and were time-consuming because of the need to ensure accurate adjustment of the levels for each observation. However, with the aid of automatic pressure control, constant pressure was maintained at each point of observation, and with some practice it was possible to obtain readings with an error not exceeding 0.1 mm. of mercury, as shown by comparative readings.

<sup>1</sup> Apiezone-A and Apiezone-B (J. Biddle and Co., Philadelphia, Pa.).

Readings of the simple mercury U-manometer were accurate to about 0.3 mm.

Calculated values in Table I were obtained by dividing the oil readings by the ratio of density of mercury at the room temperature to that of oil at the same temperature.

TABLE II. RATIO OF DENSITY OF MERCURY TO OILS

Oil Used	Equivalence of 1 mm. Hg in Terms of Oil			
	At 20° C.	At 25° C.	At 30° C.	At 35° C.
Apiezone-B	15.54	15.58	15.63	15.67
Apiezone-A	15.55	15.59	15.64	15.68
Mineral oil	15.73	15.78	15.83	15.87

In Table II are given data on the equivalence of mercury to oil readings at the temperatures indicated.

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# Improved Trap for Moisture Determination by Distillation

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IN DETERMINING moisture in materials by distillation with an immiscible liquid, certain advantages are to be gained by the use of a liquid heavier than water. In the case, for example, of tetrachloroethylene (1) the high specific gravity of the solvent permits most of the materials to be dried to float at the top of this liquid, preventing localized overheating and charring which frequently take place when lighter distilling liquids are used, and (2) there is complete freedom from fire hazard.

Because the water which is to be measured floats on top of the distilling medium in the trap, when liquids heavier than water are used for this purpose, it is not possible to effect the necessary return of solvent to the boiling flask by means of overflow, as in the Dean-Stark trap, and a different principle must be employed. A trap to effect this result has been described by Bailey (1) in which a tube connects the boiling flask with a stopcock sealed into the bottom of the graduated trap. In operation, when steady conditions have been reached, the stopcock is opened just enough to permit the distilling medium to return to the boiling flask at the same rate it is received into the trap from the condenser.

In using the Bailey trap one primary difficulty confronted the authors. Because of unsteady and widely fluctuating thermal environment, which was not susceptible of easy control, constant manipulation of the stopcock was required during a determination to prevent complete drainage of the trap or the overflow of the water at the top. This difficulty led them to produce the trap pictured in Figure 1, in which all trouble from unsteady thermal conditions was eliminated. Once the water has been received in the trap it is impossible for it to return to the boiling flask under any reasonable conditions of heating. When the apparatus has been set up and the heat applied to the flask, no further attention is required until the completion of the distillation.

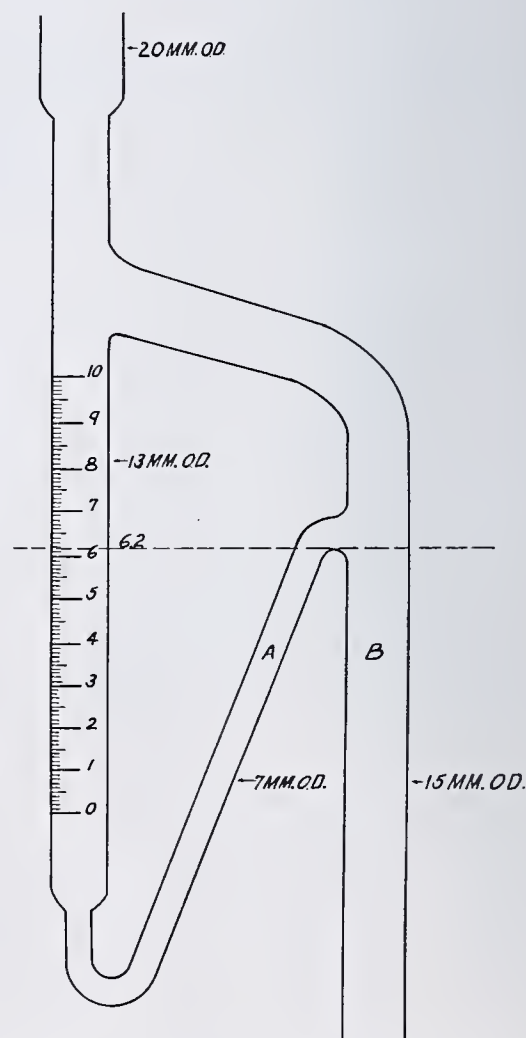


FIGURE 1. DIAGRAM OF RECEIVING TRAP



In its basic principle this trap is similar to that used for determining crankcase dilution according to A. S. T. M. method D322-35. It has been modified to accommodate it to the different specific gravities of the liquids employed.

### Design of Trap

The diagram, Figure 1, is self-explanatory in all but one particular. The entrance of reflux return tube *A* into vapor tube *B* should be fixed at a specific point peculiar to the distilling medium used. This point is determined by the ratio of the specific gravity of water to that of the distilling liquid employed. This ratio, multiplied by the number of milliliters in the entire graduated portion, gives the milliliter reading opposite which the lower point of the reflux return tube junction with vapor tube *B* should be. In the case of tetrachloroethylene, having a specific gravity of 1.6, this ratio is 0.62, and hence, with a 10-ml. trap, the point of entry of the return tube should be opposite the 6.2-ml. mark, as is shown in the diagram. Unless this junction is so placed, with some volumes of water, near the maximum capacity of the apparatus, one meniscus will be off the graduated portion.

### Reading of Meniscuses

To determine the volume of water distilled over from the sample two meniscuses must be read: an upper water-air interface, and a lower water-tetrachloroethylene junction. The reading of the upper water-air meniscus in both the Bailey trap and the authors' was rendered difficult because a drop of tetrachloroethylene customarily remained suspended upon the top of the water layer, apparently because of the surface tension of the water. Such a drop is shown clearly in Figure 2*A*, at the upper meniscus. Shaking and bumping seldom served to dislodge this drop in its entirety and another expedient was necessarily employed.

When the distillation was completed and the water in the trap had cooled to about room temperature, the condenser was disconnected and swung aside. One very small drop of a surface tension depressant, Tergitol 4 (2), was added carefully from a capillary dropper. This served immediately to cause the pendant drop of tetrachloroethylene to be released from the water surface, rendering the water-air meniscus entirely normal and easily read (Figure 2*B*). The reading should be taken rather soon after the addition of the Tergitol 4; otherwise a tendency to clouding on standing renders the reading difficult. The volume of water is not measurably increased by the addition of the necessary amount of surface tension depressant. Another material of similar nature, Tergitol 7, did not appear to be suitable for this purpose.

TABLE I. DETERMINATION OF WATER

Sample	Amount Taken	Water Found		
		By tetrachloro-ethylene %	By toluol %	By oven at 105° C. %
Water	8 ml.	99.75 <sup>a</sup>	..	..
CuSO <sub>4</sub> ·5H <sub>2</sub> O	20 grams	27.2	27.0	..
Starch	50 grams	13.36	13.4	13.5

<sup>a</sup> Recovery in trap 7.98 ml.

A second beneficent effect of the Tergitol 4 addition was noted at the lower water-tetrachloroethylene meniscus. Before the addition of this agent the meniscus here is concave downwards, and for a water-calibrated trap the reading must be taken at the cusp of the crescent. This concavity is noticeable at the lower meniscus in Figure 2*A*, but is less pronounced than is frequently the case. In order to secure contrast for photographic purposes, it was necessary to color the tetrachloroethylene with lampblack in oil, and this coloring material showed a tendency to level out the interface. However, upon adding the drop of Tergitol 4, this lower meniscus flattens out and a perfectly level interface obtains when the proper amount of the surface tension depressant has

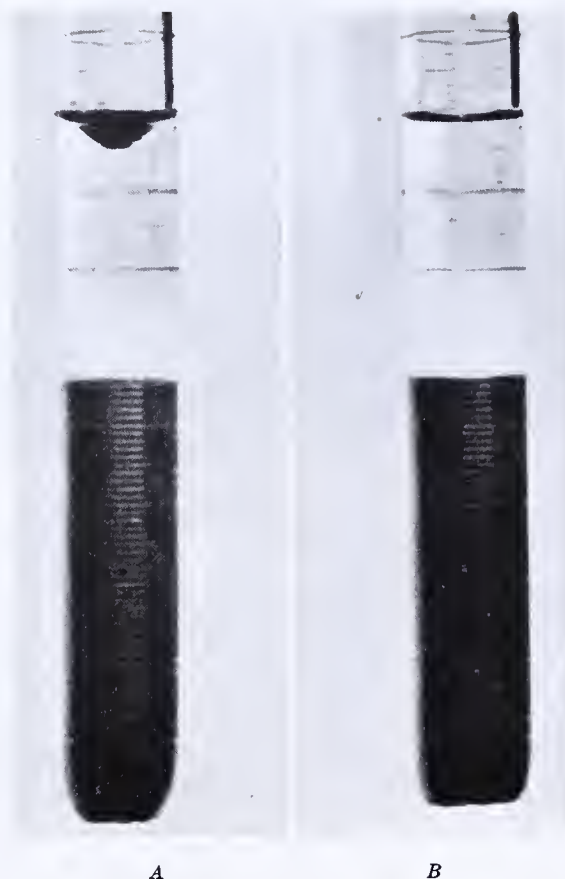


FIGURE 2. RECEIVING TRAP CONTAINING WATER

A. Before addition of Tergitol  
B. After addition of Tergitol

been added. This junction is extremely easy to read, as is apparent from Figure 2*B*, and in conjunction with the familiar water-air meniscus at the top renders the determination of the volume of water entirely satisfactory.

### Accuracy and Precision

The accuracy of the method has been determined by measuring the volume of water recovered in the trap when a known volume of water is added to the flask and distilled over (Table I). The precision of the method has been determined against two standard methods with one material, and against one standard method with another. These data are also given in Table I. The percentage of water found in the copper sulfate is slightly lower than the theoretical for 4 molecules of water (28.8 per cent), which should come off at the temperature of boiling toluene or tetrachloroethylene. Since the two methods check well on this determination, the obvious explanation is that the crystals used were slightly dehydrated, but this point has not been determined.

The trap may be calibrated so as to require the reading of only one point to render the volume of water directly rather than by the difference of two readings. A consideration of the nature of the balance between the column of tetrachloroethylene in the reflux return line and the water-tetrachloroethylene column in the graduated portion indicates that for any given volume of water between zero and 10 ml. the lower (water-tetrachloroethylene) interface will be at some point between zero and 6.2 ml. on the graduated scale, and that the location of this point will be dependent upon the volume of water present. Hence, if the point now marked zero is marked 10 ml., the present 6.2-ml. point is changed to zero, and the intervening space is graduated, a single reading will suffice to indicate the volume of water. Two disadvantages of this method of calibration should be pointed out: The accuracy of the reading will be conditional upon a constant



ratio of specific gravities between the water layer and the tetrachloroethylene layer; and any change in the ratio will vitiate the reading. Furthermore, the scale is shortened in length which in turn renders the reading somewhat less accurate.

### Summary

A trap is described which is suitable for use in determining moisture by distillation with immiscible liquids heavier than

water. Its operation is independent of thermal environment, and requires no adjustment of reflux rate. The use of a surface tension depressant facilitates the correct reading of the water volume.

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RECEIVED March 22, 1938.

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## An Easily Constructed Orifice

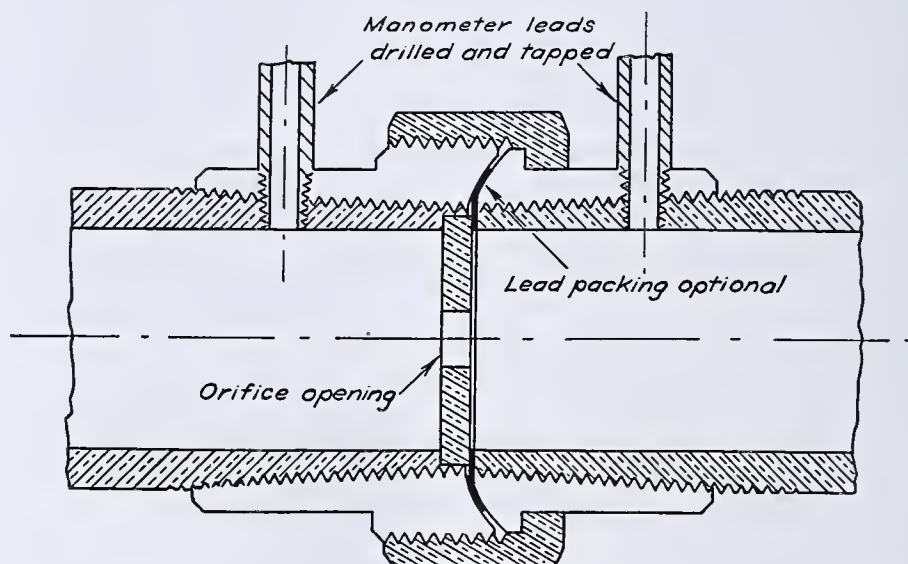
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THE velocity of a fluid in a pipe line may be determined by inserting an obstruction and measuring the change in static pressure resulting from the change in the velocity produced by it. The relationship between the size of the obstruction and the pressure drop is convertible into the line velocity. The standard orifice makes use of this principle.

can be drilled and tapped without difficulty after the other parts have been assembled.

The orifice described can be constructed from ordinary pipe fittings with the minimum of shop equipment. The interior of the orifice chamber is smooth without expansion and contraction areas near the manometer openings. The



A type of orifice construction which has been found very satisfactory is shown in the drawing. A close examination will reveal that the flanged castings of the standard orifice have been replaced by an ordinary union threaded throughout its length with a shoulder formed by the pipe in the female side to hold the orifice plate. The threaded straight sections of pipe extend to the orifice plate. The pipe ends may be machined or a lead gasket used to make a water-tight bearing between the pipe and the orifice diaphragm. Proper machining will allow the orifice plate to be held rigidly and at the same time not lose the advantage of the ground joint of the union. When a lead gasket is used, a tight joint can be made which is satisfactory at low pressures. Manometer openings

orifice plate can easily be removed and the fluid allowed to flow through the line without the resistance of the orifice. The centering of the orifice ceases to be a problem in this type of construction, once the orifice opening has been made in the exact center of the disk which serves as the orifice plate. Care should be taken as with other types of orifices to insert it in a straight pipe of sufficient length to equalize the turbulence caused by fittings such as elbows, tees, etc. The authors have found this type of orifice to be easier to construct, less expensive, and more accurate than others which use castings to form the orifice chamber.

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# Microchemical Laboratory of the Biochemical Research Foundation of the Franklin Institute

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THE construction and function of a number of microchemical laboratories have recently been described (4, 5, 6, 9, 10). These articles distinctly show the importance of microchemical methods in various fields of research, and indicate the necessity for adequate facilities in carrying out such delicate analytical work. Recognizing the value of applied microchemistry for biological research, the Biochemical Research Foundation of the Franklin Institute established a special group for the purpose of carrying out most of the analytical work by means of micromethods.

An extensive report on the construction and function of this microchemical laboratory has been published (3, 7). A condensed review is given here, indicating the principles according to which the laboratory has been set up.

In planning the laboratory, and selecting the equipment, careful consideration was given to the requirements of the foundation (8), so that the microchemical work could be correlated to that of the various research groups.

The aims and purposes of the microchemical department are as follows:

1. All new compounds or other products resulting from the research of the different groups are analyzed by the department, excepting those cases in which the analytical work constitutes an integral part of the research problem. Because most of the problems are related to the fields of organic and biological chemistry, the need for organic analytical procedures was apparent. Nevertheless it was decided to include facilities for carrying out the more important qualitative and quantitative inorganic procedures as well.

The need for microchemical methods arises not only from the frequent scarcity of material (often less than 20 mg.), but also from the time saving which can be effected by microanalysis. The latter is especially important when the different steps of a given reaction or fractionation must be closely followed at frequent intervals.

2. In addition to carrying out the above analytical work, the microchemical department functions as an advisory group in analytical problems in general.

3. Research in the field of applied microchemistry is also carried out. Frequently the efficiency of standard procedures must be controlled, particularly when impure samples of biological origin are being analyzed.

## Description of the Laboratory

The microchemical laboratory is located on the fifth floor of an office building. The rooms had not previously been used for chemical work; this was of some advantage, since special equipment could be designed and arranged so as to utilize fully the available space. Proper distribution, ac-

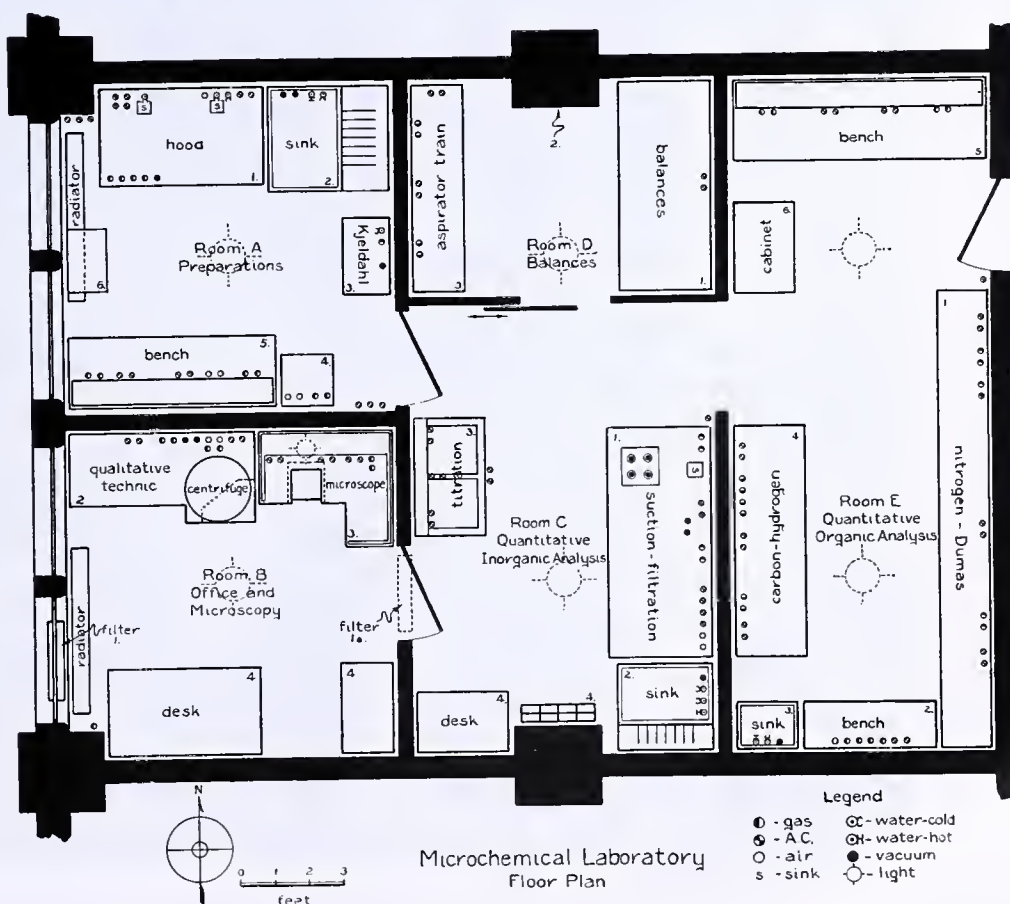


FIGURE 1



cessibility, and convenience of laboratory furnishings and special apparatus are of primary importance in this type of work. Only in this way can strain to the microanalyst be avoided and high working speed maintained.

Figure 1 shows the floor plan of the laboratory, which is divided into five sections:

Room A is for preparative work, decomposition of samples including Kjeldahl procedures, and all manipulations which require a hood, so as to avoid corrosion of finer apparatus in the other rooms.

Room B, for qualitative microtechnics and microscopical investigations, serves at the same time as an office and reference room. All inorganic and organic qualitative and semiquantitative analyses, mechanical separations under the microscope, and technics connected with chemical microscopy are carried out here.

Room C is used for drying samples *in vacuo*, filtration procedures in quantitative work, and microtitrations.

Room D is separated from room C by a plywood wall only, and serves as a balance room.

Room E is equipped for quantitative organic elementary microanalysis and electrolytic procedures, and has ample space for special apparatus which can be set up if needed (benches 2 and 5 in Figure 1).

A few of the furnishings in this laboratory are described below in some detail, as they may be of special interest to other microchemists.

**WORK BENCH FOR QUALITATIVE MICRITECHNICS.** For all qualitative inorganic and organic microchemical analyses and micropreparative procedures, a unit has been formed consisting of a microscope table and a work bench. This unit, located in room B, is arranged so that all necessary equip-

ment is conveniently at hand, and unnecessary movements and distractions can be avoided. This is of particular importance in qualitative microanalysis, since otherwise the advantages over the ordinary methods become questionable. Nearly all samples submitted for quantitative analysis are subjected to a preliminary qualitative or semiquantitative organic elementary analysis, so that the correct procedure, sample weight, etc., may be selected according to the amounts of constituents and impurities present (1).

The microscope table was built by E. H. Sheldon and Co., Muskegon, Mich., according to drawings obtained through the courtesy of the Bell Telephone Laboratories, Inc., New York, N. Y. The work bench for all qualitative technics was specially designed (Figure 2) and is rather unusual.

On its right side a hand centrifuge with a special head for micro centrifuge cones and capillaries is fixed to the table, the top of which is covered with gray linoleum. The centrifuge is surrounded with a protecting shield and cover; its projecting handle is set into a small quadrant, thus eliminating accidental knocking. Two "music room" bulbs are mounted on the under side of the lowest shelf for reagent bottles, etc., providing uniform illumination without shadows from the fingers and body of the analyst. On the left side a special reagent block with 5 tiers of holes serves for vials filled with various reagents for qualitative organic analysis.

The drawers of the table on the left side are arranged for incoming samples, for all small apparatus in the spot test technic, and for working tools. Over the kneehole is a wide drawer for slides, cover glasses, forceps, etc. On the right side are 7 narrow compartments containing the liquid reagents for the qualitative organic elementary analysis, capillaries, pipets, glass rods, platinum loops, wires, and spatulas, etc. In the section of the bench below the centrifuge are drawers, one of which is provided with a special rack for the various micro centrifuge cones; the other



FIGURE 2. WORK BENCH FOR QUALITATIVE MICRITECHNICS



drawers contain separatory funnels, specific gravity pipets, and microapparatus for extraction, sublimation, and distillation, all of which are thus kept dust-free and ready for immediate use.

**WORK BENCH FOR SUCTION, FILTRATION, AND VACUUM DRYING.** A suction plate similar to the one described by Clarke and Hermance (5) is inserted in the linoleum-covered table top of this bench in room C (Figure 3).

In the vacuum line leading to this plate lie two outlets to which are connected the different filter devices and the filter tubes in their drying blocks as used in quantitative microanalytical work; a few of these arrangements are shown in the center of Figure 3. Six needle valves allow the independent use of each of these suction areas. The high-vacuum pump is located in the right cupboard of the bench on a wooden case, which rests on 6 rubber stoppers to reduce the otherwise very annoying vibrations through the floor.

A few permanent pieces of equipment are placed on this table, one of which is the Abderhalden dryer on the extreme right side. It is provided with a special metal rack designed by Alber (2) for opening and closing charging tubes with ground caps without bringing the sample into contact with moist air. Another drying apparatus for use with high vacuum, described by Unterzaucher (11), is supported by one of the Kewaunee buret rods with standard taper, which are successfully used on the other tables. In this laboratory it is very important to dry the samples under carefully controlled conditions, since many of the biochemical products are extremely hygroscopic; only by preventing any access of (moist) air can accurate results in the various determinations be obtained. The big shelf carries, in special metal holders, the micro wash bottles, the flasks with interchangeable ground joints which contain liquids of constant boiling point for use with the Abderhalden dryer, etc.

**TITRATION TABLE.** For microtitrations a special table has been designed for use under widely varying conditions. This equipment offers the possibility of changing the illumination

according to the type of titration, and provides for the future use of ultraviolet light necessary with fluorescent indicators. Figure 4 illustrates this table.

Inserted in the top are two removable glass plates which are illuminated from underneath. The two bulbs on each side are connected to one sliding resistance, which allows dimming the light gradually. Colored light filters of Pyrex glass are interposed in the slits below the top by means of wooden holders. The color effects help considerably in observing weak end points by producing sharper color contrasts. The heat from the bulbs is carried off by means of slits in the side walls of the table. Accurate readings of the meniscus of the standard solutions in the microburets is made easier through two uniformly illuminated glass plates which are mounted in the back of the burets. Besides the standard microburets, other micro- or macroburets can be supported by clamps from the three metal racks, which also serve as supports for covers—e. g., when work in ultraviolet light is to be done.

**BALANCE ROOM.** This room should be air-conditioned, with a constant humidity of about 50 per cent, a constant temperature of about 24° C., completely dust-free, and free from vibrations, in order to provide ideal surroundings for such delicate weighings (6, 9, 10). It was impossible to provide all these features in the laboratory at the present time, the only precaution taken being the installation of a filtering device (Air-Pilot) in room B for the removal of excessive dust from the city air. For the microbalances a space centered in the laboratory was selected and protected as far as possible from the influence of sudden temperature fluctuations by separating it from the other room with a plywood wall and a gliding door. The vibrations which, for instance, come from the motor for compressed air on the floor just above the balance room are eliminated by the special construction of the balance table.

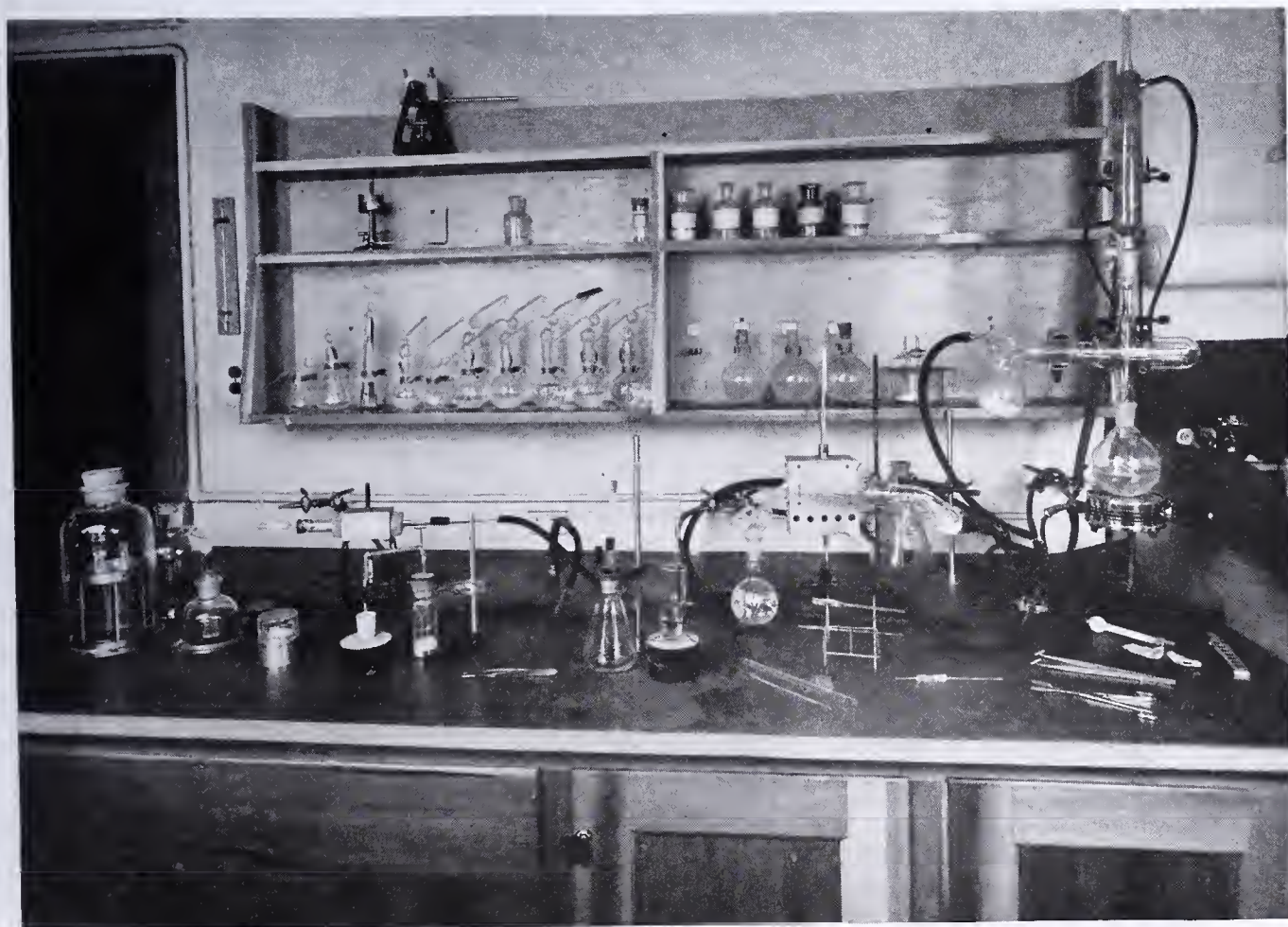


FIGURE 3. WORK BENCH FOR SUCTION, FILTRATION, AND VACUUM-DRYING PROCEDURES



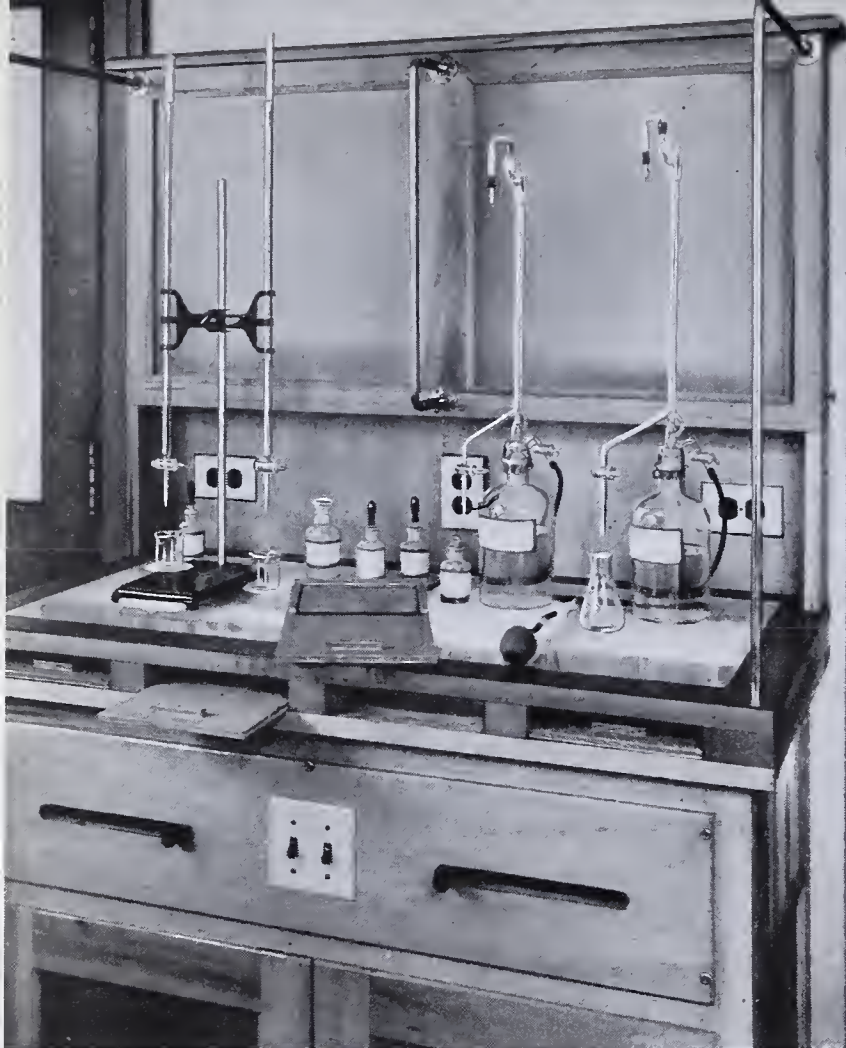


FIGURE 4. TITRATION TABLE

This table has an oak top 2 inches thick, which is supported by two triangular iron brackets. These are inserted into the wall and partly insulated from vibrations of the wall by cork plates 1 inch thick. Between the table top and the iron brackets, lead sheets 0.5 inch thick are interposed to break up remaining short shocks and vibrations coming from the wall; the table top itself has no direct contact with the walls. In order to take care of the long vibrations and short shocks which are not absorbed by the above-mentioned breaking devices, the microchemical balance has further supports: a rubber pad, 1 inch thick, is placed directly on the table, and a heavy marble plate rests upon it. Onto the marble plate are glued, in the position of the feet of the balance, three metal rings filled with rubber, on top of which are placed round aluminum sheets having no direct contact with the metal rings, the whole serving as a shock-free support. To prevent vibrations which may result from writing directly on the balance table, classroom-type chairs with side arms are used for recording the results at the balances. With these arrangements, no disturbances in weighing at the two Kuhlmann microchemical balances are noticeable.

WORK BENCH WITH DRAWERS FOR STORING WEIGHING VESSELS AND CORRESPONDING TARES. A very useful arrangement for keeping the micro weighing vessels and the corresponding counterpoises in place is incorporated in the work bench in the balance room (Figure 5). It is a general rule in microanalysis to tare any of the vessels to be weighed on the microchemical balance with an object which has similar shape, the same density, and a weight about 1 to 2 mg. less than the vessel. With three microanalysts, the unavoidable accumulation of the numerous tares in the balance cases and around the balances could easily result in mistakes. The drawers of the work bench in Figure 5 contain wooden blocks with openings corresponding in shape to

each vessel and its counterpoise, so that they are ready for immediate weighing when needed and are protected from dust.

### Efficiency of Laboratory

In the opinion of the authors, the above construction fulfills all the requirements for a very useful and efficient microchemical laboratory. The various pieces of special equipment are, naturally, not without precedent. The experience leading to this final form of construction was obtained through setting up five other microchemical laboratories for various purposes in different countries and by visits to well-established microchemical laboratories in this country. It is hoped that this abstract of the original paper (3) will be helpful to other workers who may be concerned with the problem of equipping a microchemical laboratory.

The best proof of its efficiency is the statement in a report given by the director of the foundation (7), that all incoming problems, which vary considerably because of the wide scope of research done in this foundation, can now be solved without delay.

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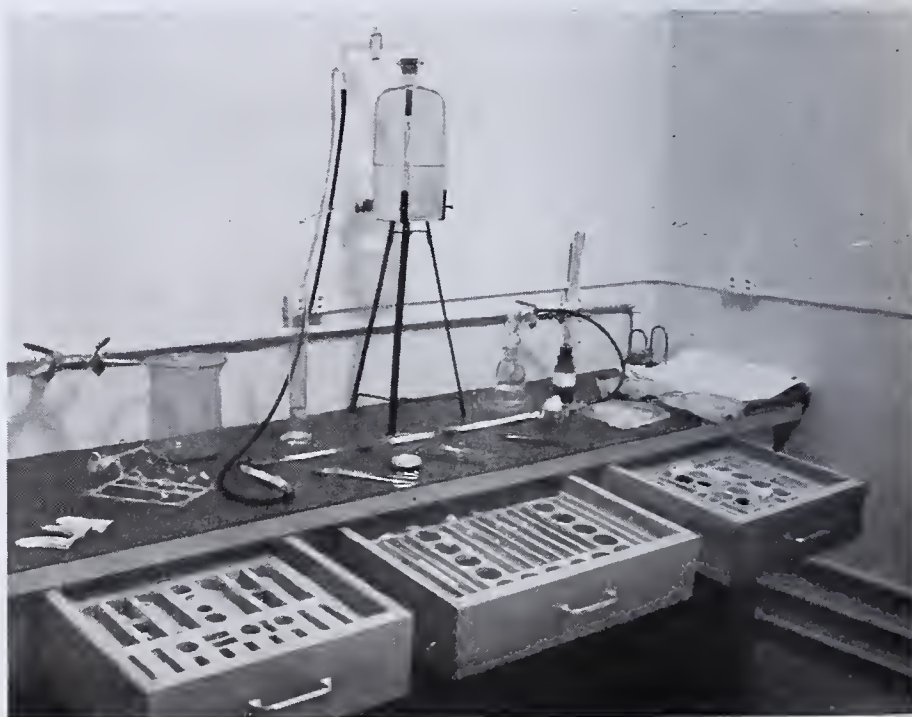


FIGURE 5. WORK BENCH WITH DRAWERS FOR STORING WEIGHING VESSELS AND CORRESPONDING TARES



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Quantitative Analysis Based on Spectral Energy

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An explanation is given for certain limitations of the commonly used internal standard method, and energy of spectral emission is suggested for measurement of concentration in place of intensity. Experimental work shows that the energy of spectral emission in a carbon arc is directly proportional to the weight of element causing the emission. For quantitative analysis, therefore, it is only necessary to determine

energy per unit weight of element on known samples, and apply this value in the analysis of unknowns.

This procedure permits working over the entire range from the lowest limit of sensitivity up to 100 per cent. The presence of other elements appears to have no effect on the analysis. The average error was found to be 8.3 per cent and the maximum error was 18.5 per cent.

THE concept of intensity is as old as spectroscopy. We speak of lines as being intense or faint. Although we now use for observation the photographic plate, an integrating device, we still use the terminology appropriate to the spectroscope, an indicating device. It was natural, therefore, when the spectrograph came to be used for quantitative work, to apply this idea of intensity of an emission spectrum as a parameter of concentration.

The use of spectral intensity for analysis carries the implication that it is a property which varies only with the concentration. It is well known that a great many other factors affect intensity, so that it is necessary to impose the requirement that all conditions of the experimental procedure be held constant; the conditions here referred to are the current, optical setup, exposure time, photographic routine, and composition of sample. This last requirement is manifestly impossible to control, for this is the very thing we are trying to determine. Intensity methods have, therefore, purely from trial and error experience, been restricted in the main to so-called "simple samples" and low concentrations (such as the determination of impurities in metals of high purity) in which the composition of standards and unknowns is very nearly the same.

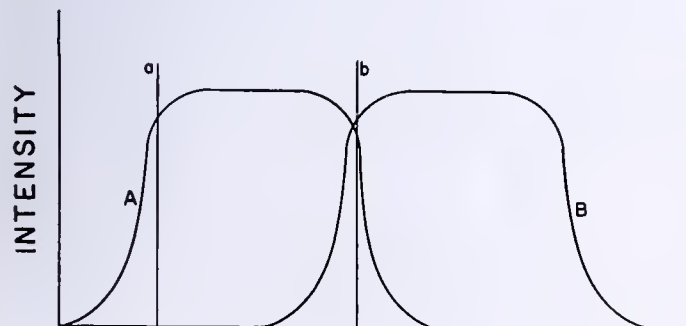


FIGURE 1

The literature of recent years contains several observations (1-4) to the effect that the various elements present in the arc (the spark has similar faults) do not emit their spectra simultaneously, or at a definite and constant intensity, but on the contrary show very wide variations, depending on the elements which make up the sample. The arc behaves like a small furnace, which in fact it is, volatilizing the substances in it in the order of their relative vapor pressures, the more volatile coming off first and the more refractory last.

How strikingly abrupt and clear-cut this differential volatilization may be is very well shown by Goldschmidt and Peters (2). They placed a partly cuped lead bead containing silver, gold, and the six platinum metals in a carbon arc and completely vaporized the sample. The plateholder was shifted periodically during this process, allowing 20 seconds for each exposure and 5 seconds for the shift. The plate showed the lines of the nine metals in this order:

Seconds	Pb	Ag	Au	Pd	Ru	Rh	Pt	Ir	Os
0 to 20	Pb	Ag	Au	Pd	Ru	Rh	Pt	Ir	Os
25 to 45	Pb	Ag	Au	Pd	Ru	Rh	Pt	Ir	Os
50 to 70	Pb	Ag	Au	Pd	Ru	Rh	Pt	Ir	Os
75 to 95	Pb	Ag	Au	Pd	Ru	Rh	Pt	Ir	Os
100 to 120	Pb	Ag	Au	Pd	Ru	Rh	Pt	Ir	Os
125 to 145	Pb	Ag	Au	Pd	Ru	Rh	Pt	Ir	Os
150 to 170	Pb	Ag	Au	Pd	Ru	Rh	Pt	Ir	Os

The effect of this differential volatilization on an analytical procedure using intensity methods can best be explained graphically.

Let us examine the emission, during the course of volatilization, of some particular element of a sample introduced into such an arc. In other words, let us plot the variation of intensity of some particular line with respect to time (Figure 1). We should expect intensity to start from zero soon after the arc is struck, and gradually reach a maximum value, which would be maintained for an interval roughly equivalent to the absolute amount of the element present in the arc, and then drop back to zero again, when all had volatilized. This purely qualitative picture is represented by curve A of Figure 1.



Now if in a second sample, similar to the first and containing the same concentration of the element of curve *A*, there is present a more volatile element, say one of the alkalis, then curve *A* will be displaced to the right, as shown in curve *B*, for the alkali metal will volatilize before the more refractory one. But intensity methods assume, as they must, constancy of emission, and so their procedures consist in making an exposure for a fixed number of seconds, commencing either at the instant of striking the arc, or after a fixed interval, when it is hoped that constant conditions have been reached. This exposure is shown on the graph as the two vertical lines, *a* and *b*.

Area in Figure 1 represents energy (product of time and intensity). It is this energy that is recorded by the photographic plate as density of image, and thus the quantity measured by the intensity methods is the energy represented by the area enclosed by lines *a* and *b* and curve *A*. This procedure would be unobjectionable if the maximum of the intensity curve were reproducible under all conditions and the whole curve fixed on the time axis. But if, because of a change in composition, it shifts to, say, curve *B*, so that now the energy being recorded on the plate is represented by the area bounded by the two verticals and curve *B*, large errors result and the intensity method fails.

From these considerations it is evident that the principal cause of the trouble is the time factor entering into the exposure. Fundamentally, there is no physical relationship between intensity and mass or concentration of an element; they are two separate quantities. If we adopt a procedure involving a consistent relationship, the difficulty should disappear. With further reference to Figure 1, it seems reasonable to suppose that the total energy of the emission—i. e., the area under curve *A*, which does not contain the time factor—should prove to be a more robust parameter, not influenced by changes of composition. This is the basis of the method described in this paper.

There is considerable theoretical basis for this view. The carbon arc may be pictured as a furnace on which is set a gas-discharge tube, operating at atmospheric pressure and having walls of cool air—the surrounding atmosphere. The furnace discharges into this tube metallic vapors, whose atoms become excited and emit radiation and then pass out of the tube and out of the process. There is thus a unidirectional flow of atoms from the lower electrode into the zone of excitation and out into the cool air.

The intensity at any interval of time  $dt$  is a measure of the atoms present in the luminous zone during that interval (other conditions being the same). As the atoms are continuously lost out of the tube, while new ones take their place, the intensity integrated over the time of emission will be a measure of the number of atoms that have passed through during that time. If the time is taken from the instant of striking the arc until all the sample has burned off, the number of atoms that have passed through the zone of excitation will be the same as the number contained in the sample. Therefore, the integrated intensity,  $\int I dt$ , is a measure of the number of atoms in the sample, or of the mass of the element in the sample. The equation expressing this condition is

$$m = k \int I dt \quad (1)$$

where  $m$  is the mass of element in the sample and  $k$  is a proportionality constant.

One other factor influencing energy emitted with respect to mass should be mentioned here. Excitation in an arc, whether due to thermal action or to impacts from cathode electrons, will be directly influenced by the current passing through the arc. A larger current, therefore, will cause more excitations among a given number of atoms than a smaller one. We are using the emitted energy as a means of counting the number of atoms passing through the arc, and if this count is to be reproducible from one exposure to another, the current must be standardized for any series of comparable tests.

## Experimental

To test this hypothesis experimentally involves establishment of the validity of the above equation. It can be done in several ways; the author's procedure had, perforce, to be based on the equipment available, which consisted of a large Littrow-type quartz spectrograph equipped with a variable rotating sector, and a densitometer.

The portion of the equation at the left, pertaining to the mass of element consumed, obviously required the use of the carbon arc. Amounts of chemically analyzed samples were weighed on a microbalance and transferred with the aid of a small funnel into cored graphite electrodes. These formed the positive of the arc, and the discharge was maintained at constant current until there was no doubt that the entire sample had been consumed.

Evaluation of the portion of the equation at the right presented a much more complex problem. In the first place, the author realized that the usual method of illuminating the slit, by means of a spherical condenser, which throws a geometrical image of the source on the slit, was not suitable, because wandering of the arc would cause a corresponding shift at the slit; thus the plate would not be continuously illuminated during the whole of the exposure. A cylindrical condenser was therefore substituted (a suggestion of S. Jacobsohn, of the Gaertner Scientific Co., Chicago, Ill.), the axis of which was set perpendicular to the slit. This type of lens presented a horizontal segment of the arc column to the view of the spectrograph, so that while the light never fell outside the prism, the images of the incandescent poles were thrown above and below the slit opening, none of this light entering the spectrograph.

The integration required by the equation was to be done by the photographic plate. However, the response, which is in terms of density, had to be converted to relative energy values. The method decided upon consisted in giving each plate a series of regulated exposures, varying in intensity but constant in time, from a source that was reproducible from day to day. The source that most nearly met this requirement was a high-pressure direct-current quartz mercury-arc lamp with controlled input. The lamp and arc stand were mounted on a dovetail slide, so that either could be placed interchangeably in the optic axis of the spectrograph. The light path traversed by the standard radiation and the unknown was therefore the same. Controlled variation in intensity was obtained by means of the rotating sector, used as specified by Webb (5). This permitted the establishment of a characteristic curve (intensity scale) for each plate, from which densities could be converted into the corresponding energies, since both time and intensity of the causative radiation were known—that is, the curve expressed the relation between energy and plate response.

After development, the densities of a chosen mercury line and of a neighboring line of the unknown were measured by means of a densitometer. The mercury line densities were then used to construct the characteristic curve for each plate, and from this curve energies corresponding to the unknown's densities were read off. This is a null method, in which the unknown energy contained in a particular spectrum line is directly equated to the known energy of a mercury line, the plate being used merely as a null indicator.

A difficulty arose at this point through the inability of the photographic plate to integrate light correctly [the reciprocity error, a term applied specifically to photographic emulsions which exhibit failure of the Bunsen-Roscoe law. This failure manifests itself as unequal responses to dosages of energy which are equal, but at different intensities (or conversely, for different exposure times)]. The author was endeavoring to measure radiation of variable intensity in terms of constant radiation. Under these circumstances there is no way of avoiding reciprocity error. However, it was minimized by the use of Eastman contrast thin coated plates (recommended by the manufacturers after the problem had been presented to them), the reciprocity error of which was a minimum in the exposure time range in which the author was working, 15 seconds to 4 minutes. The plates in all cases were brush-developed, to avoid errors due to uneven development, and contrast was controlled at approximately unit gamma.

## Results

The procedure was tried out at first on simple mixtures over a narrow range. Results of these tests were so encouraging that it was then tried on a series of samples of widely varying composition and over a large range of concentrations. The



metal whose radiation was to be measured was calcium (calculated in this paper as CaO) and the samples were various minerals and rock products, several of them Bureau of Standards standard samples.

The samples, with their CaO contents, are listed in Table I.

TABLE I. SAMPLES USED

Sample No.	Principal Constituents	CaO %
1 Bureau of Standards No. 98 (plastic clay)	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	0.21
2 Bureau of Standards No. 99 (feldspar)	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>	0.36
3 Feldspar	(K <sub>2</sub> O, Na <sub>2</sub> O)Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>	0.81
4 Bureau of Standards No. 102 (silica brick)	SiO <sub>2</sub>	2.29
5 Bureau of Standards No. 104 (burnt magnesite)	MgO	3.35
6 Feldspar	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>	4.46
7 Tremolite-talc	CaO, MgO, SiO <sub>2</sub> (complex)	7.58
8 Tremolite-talc	CaO, MgO, SiO <sub>2</sub> (complex)	9.18
9 Dolomite	CaO·MgO·2CO <sub>2</sub>	34.02

Each sample was run in quadruplicate. In order that all exposures should fall within the latitude of the plate (it was not necessary that they fall only on the straight-line portion of the characteristic curve) the intensity was varied by means of the rotating sector, the transmission being successively reduced with increasing CaO content. The results were then calculated to a basis of 100 per cent transmission, to make all exposures comparable.

TABLE II. RESULTS OF QUADRUPLICATE EXPOSURES

Sample No.	Weight of Sample Gamma	Weight of CaO Gamma	Energy, Arbitrary Units	Sector Transmission %	Energy at 100 Per cent Transmission
1 a	24,300	51.0	3.1	10	31
b	23,400	49.2	2.2	10	22
c	31,200	65.5	3.1	10	31
d	28,000	58.8	3.1	10	31
2 a	25,700	92.5	2.6	5	52
b	26,100	94.0	2.65	5	53
c	25,500	91.8	2.65	5	53
d	28,500	102	3.0	5	60
3 a	28,800	233	7.4	5	148
b	26,300	213	6.6	5	132
c	21,400	173	5.3	5	106
d	26,200	212	6.8	5	135
4 a	30,100	690	10.0	2.5	400
b	34,400	788	10.7	2.5	428
c	34,800	797	11.0	2.5	440
d	31,400	720	9.8	2.5	392
5 a	29,900	1,000	9.1	1.5	606
b	24,500	820	8.0	1.5	533
c	28,900	968	8.8	1.5	587
d	28,800	965	8.7	1.5	580
6 a	28,600	1,273	18.8	2.5	753
b	29,500	1,315	18.0	2.5	720
c	25,500	1,135	15.5	2.5	620
d	21,200	945	Lost	2.5	Lost
7 a	27,900	2,110	16.3	1.5	1,088
b	21,100	1,600	13.0	1.5	866
c	22,900	1,740	12.5	1.5	833
d	27,800	2,110	15.0	1.5	1,000
8 a	24,800	2,280	11.6	1.0	1,160
b	20,800	1,914	10.7	1.0	1,070
c	22,700	2,080	10.9	1.0	1,090
d	22,600	2,075	10.2	1.0	1,020
9 a	26,700	9,080	43	1.0	4,300
b	21,600	7,350	38	1.0	3,800
c	21,300	7,250	34	1.0	3,400
d	20,800	7,070	33	1.0	3,300

The results are collected in Table II. Column 1 contains the sample numbers, corresponding to Table I. Column 2 shows the weight of sample placed in the cores of the electrodes. Column 3 shows the weight of CaO present in each sample (weight × per cent CaO). Column 4 is the energy, in arbitrary units, as read from the density curve of the standard radiation plotted for each plate. Column 5 shows the transmission setting used to obtain the values of column 4. Column 6 is the calculated energy at 100 per cent transmission (figures of column 4 divided by figures of column 5).

The calcium line on which the measurements were made was at 3179 Å., the mercury line was at 3125 Å. The spectra for the lower concentrations of CaO showed background. The energy values for these tests were high, indicating that background correction was necessary. This was accomplished by converting the density readings of background, taken adjacent to calcium 3179 Å., into energy values by means of the mercury curve, and subtracting these from the energy values obtained for the calcium line (as in column 4 of Table II). When this was done the corrected points were consistent with those obtained from background-free spectra. The figures given in column 4 of Table II have been corrected for background in this way.

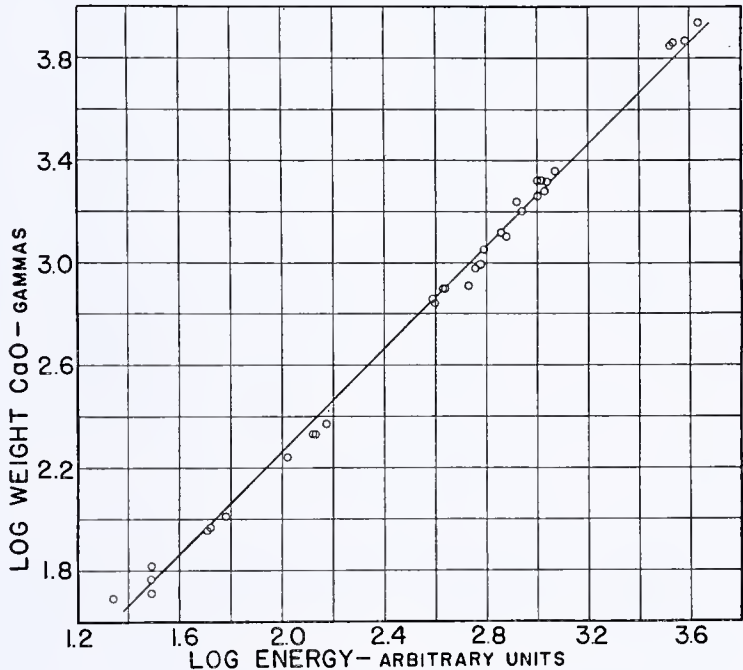


FIGURE 2

Figure 2 shows the relation between weight of CaO in gamma (a gamma is one microgram or 10<sup>-6</sup> gram) volatilized in the arc and energy of the resultant emission (in arbitrary units) plotted on a logarithmic scale. A straight line drawn at 45° to the axes fits the points within the experimental errors. The equation of such a line is

$$\log m = \log E + C \quad (y = x + a)$$

$$\text{or} \quad \frac{E}{m} = k$$

where *m* is the weight of element, *E* the energy of emission, and *k* a constant. The results therefore agree with the equation given in the introduction.

Discussion

Simply stated, the experimental work described herein outlines a method of measuring elemental masses by measuring (relative) radiation from an electric arc. It should be applicable to various procedures and instruments, but is restricted in this discussion to those in common use at present, the spectrograph and densitometer.

In the experimental work radiation was measured and compared with known mass. The process obviously can be reversed and mass determined from radiation. If we rearrange Equation 1 thus

$$K = \frac{\int I dt}{m}$$

and measure the energy ∫ *I* *dt* in any convenient units and *m* in gamma, then *K* has the meaning of so many energy units



TABLE III. VALUE OF *K*

Sample No.	<i>K</i>	Deviation (× 10 <sup>-3</sup> )	Per Cent Error
1 a	0.608	+ 58	+10.5
b	0.448	-102	-18.5
c	0.473	- 77	-14.0
d	0.527	- 23	- 4.2
2 a	0.563	+ 13	+ 2.4
b	0.563	+ 13	+ 2.4
c	0.577	+ 27	+ 4.9
d	0.585	+ 35	+ 6.4
3 a	0.635	+ 85	+15.5
b	0.620	+ 70	+12.7
c	0.613	+ 63	+11.5
d	0.636	+ 86	+15.6
4 a	0.580	+ 30	+ 5.4
b	0.543	- 7	- 1.3
c	0.552	+ 2	+ 0.3
d	0.545	- 5	- 0.9
5 a	0.606	+ 56	+10.2
b	0.650	+100	+18.2
c	0.607	+ 57	+10.4
d	0.602	+ 52	+ 9.5
6 a	0.592	+ 42	+ 7.6
b	0.548	- 2	- 0.3
c	0.547	- 3	- 0.5
d	Lost	...	...
7 a	0.515	- 35	- 6.4
b	0.542	- 8	- 1.4
c	0.480	- 70	-12.7
d	0.474	- 76	-13.8
8 a	0.508	- 42	- 7.6
b	0.560	+ 10	+ 1.8
c	0.525	+ 25	+ 4.5
d	0.492	- 58	-10.5
9 a	0.473	- 77	-14.0
b	0.517	- 33	- 6.0
c	0.470	- 80	-14.5
d	0.467	- 83	-15.1
Av.	0.550	45.8	Total 291.5
Av. error		8.3%	8.3%

per gamma of element. This has been done and the values so obtained are listed in Table III. The average so obtained, *K* = 0.55, for calcium 3179 Å. with a current of 12.5 amperes, should therefore be a constant for that particular line dependent on the lamp used and the arc current, and apparently on no other factors.

With the constant *K* thus established, the concentration of an element in a mixture can therefore be determined by means of the equation

C = E / KM

where *M* is the weight of sample taken in gamma.

It is apparent that this method based on total energy has several marked advantages over the customary intensity methods. It eliminates at one stroke all the difficulties inherent in the use of an internal standard; finding a suitable pair of lines for one concentration range and another pair for another range; knowing the ratio between unknown and base material; the necessity that both these metals volatilize at the same rate and during the same portion of the exposure; and the necessity of preparing an extensive series of graduated standards to fix the calibration curve.

So much for the negative virtues. On the positive side may be mentioned the ease with which the working constant may be evaluated, requiring but one or two standards; the consequent saving of time, permitting the method to be used for research or occasional samples; the ability to handle samples of any concentration without altering the procedure; and the possibility of correcting for background.

Data are here presented for a single line of a single metal. But the writer's experience, so far as it has gone, indicates that any line of any metal can be used for quantitative work, that any line will show this constant relation between mass and energy. Anomalous effects, such as are usually ascribed to "arc and spark lines," have not been detected. The choice of line is governed only by convenience.

To study the influence of one type of atom on the excitation of another type has been one of the objects of the experiment, but no such influence has been detected within the resolution of these measurements. Three of the samples used (the feldspars) contained considerable concentrations of sodium and potassium. The view is generally held that the presence of alkalis in the arc changes the intensity relationship in the spectrum. For instance, Harrison (3) says, "The alkali metals have unusually low ionization potentials, so their presence in quantity in a sample tends to suppress the excitation of other atoms." This was not the author's experience, for these three samples are consistent with the others. These samples were included in the series because of this general opinion that the alkalis are the worst offenders; if they did not affect the excitation of the calcium atoms under the conditions of the author's procedure, it was felt that no other elements would.

Two other samples may be mentioned in this connection. In No. 4 the calcium is present in an SiO<sub>2</sub> base and in No. 5 in an MgO base. These also showed no inconsistency. It is of course unsafe to make the categorical statement, based on such meager data, that the various atoms have no effect on each other; this point can be settled with assurance only by extensive work with various combinations. It is perhaps unnecessary to remark that lines terminating in the ground state should be used with caution for quantitative work, because of their tendency to show reversal.

As to accuracy, here also the comparison is favorable. The accuracy obtainable with the best of the intensity methods is of the order of 5 per cent error for a single determination. The errors for the data of this paper have been calculated and are shown in column 4 of Table III. These are higher than should be expected in an actual analysis, as the data have been taken over a much greater range than will usually be experienced in practice. Some reciprocity error has been unavoidable (as evidenced by the slight concavity of the series of points towards the log weight axis, Figure 2). Also, errors in chemical analysis, while small, had some effect on the results. Probably further experience will show that synthetically mixed samples are simplest and best. The error, then, should be found in practice to be of the same order as the most refined of the present methods.

A principal difficulty of the total energy method is with the standard light source. Of the two sources commonly available with sufficiently high reproducibility to be useful, the incandescent lamp and the mercury arc, neither is entirely satisfactory. The former can be used only from the infrared to about 4500 Å., and even in this range the change of intensity with wave length is sharp. Filters could conceivably equalize this fault, but only at the expense of reduced intensity, which is already too low compared to the monochromatic intensity of arc lines. (It must be remembered that exposure time cannot be increased without limit, but must be comparable to emission time of the element under investigation.) The principal fault of the mercury arc lamp is the paucity of lines in the mercury spectrum. A procedure that does away with the necessity for a standard lamp, but which is suitable only for occasional samples, has been tried in this laboratory. It consists in photographing the spectra, on the same plate, of a series of known samples and of the unknown, the weights of all samples being taken. The density of a particular line in each of the known spectra is measured and these values are plotted against log weight of element in the knowns. The densities of the unknown samples are then interpolated in this curve (which should be a straight line if the densities fall on the straight-line portion of the characteristic) and the unknown weight of element thus read off. This, divided by weight of sample taken, gives the concentration.

It appears possible, from the relation between mass and



emitted radiation found here, to devise a method which dispenses with both the photographic step and the standard lamp. For instance, the radiation from the arc, as an analyzed sample of known weight is volatilized, can be dispersed by a monochromator and a chosen line allowed to fall on a suitable radiation measuring device (photocell, thermopile, etc.). The response could then be integrated over time of emission by some such means as a photon counter and the constant *K* thus determined. Investigation in this direction could possibly lead to the development of a practical device for chemical analysis by purely mechanical means—an analytical machine. It is hoped that this phase of the problem will be attacked when more experience with the general procedure has been acquired.

The work described here is part of a broader research by the Nonmetals Division of the Bureau of Mines, having in mind the adaptation of quantitative methods of spectrochemical analysis to the nonmetallic minerals. Orthodox chemical methods, even for constituents occurring as com-

monly as titania and zirconia, are so long and difficult that there is room for much improvement.

Acknowledgment

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Determination of Sugars in Plant Materials  
A Photocolorimetric Method

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FOR several years the method used in this laboratory for the determination of reducing sugars in plant materials has been a combination of the Quisumbing-Thomas (1) and the Shaffer-Hartmann (7) methods. Cuprous oxide was precipitated according to the former method and determined directly without filtering according to the titration procedure described by the latter. The results have been fair, but the procedure possesses many disadvantages, such as the time and extreme care required for determinations, the number of reagents necessary, and the large amount of plant material low in sugar which must be extracted in order to obtain enough sugar for an analysis.

Several quantitative methods for reducing sugars have been based on the reduction of ferricyanide to ferrocyanide. In Strepkov's method (8) for the microdetermination of carbohydrates in plant materials, the excess ferricyanide was determined by an iodometric titration. Hassid (4) determined quantitatively the ferrocyanide formed by titration with a standard ceric sulfate solution. In a procedure for the determination of glucose in blood and urine, Hoffman (5) made use of the fact that ferricyanide solutions are yellow whereas ferrocyanide solutions are colorless. Glucose was thus estimated by measuring in a photoelectric colorimeter the diminution in yellow color of an excess of ferricyanide. The present author has adapted this method to the determination of reducing sugars in plant materials. The method is rapid and accurate, the procedure is simple, and only one standard solution is necessary. Precise results can be obtained with samples containing from 0.05 to 0.4 mg. of reducing sugars.

Solutions and Apparatus

ALKALINE FERRICYANIDE REAGENT. Potassium ferricyanide (1.8000 grams), purified according to Peters and Van Slyke (6), and 40 grams of anhydrous sodium carbonate were made up to 1 liter with distilled water. When kept in an amber-colored bottle and stored in a dark place, this solution remained stable

for 3 months. In order to be sure that the solution had not deteriorated, a blank reading on the reagent was made with each series of determinations.

The photoelectric colorimeter used was a Cenco-Sheard-Sanford photometer equipped with a blue filter and 12-cc. absorption cells.

Description of Method

CALIBRATION OF PHOTOELECTRIC COLORIMETER. Two cubic centimeters of solutions containing from 0 to 0.4 mg. of pure glucose were placed in test tubes or centrifuge tubes marked for 15 cc. Exactly 3 cc. of the alkaline ferricyanide reagent were added to each tube. The tubes were then immersed in boiling water for 5 minutes, cooled under the tap, and diluted to the mark. After mixing the contents of the tubes, the color intensities were determined in the colorimeter set at 100 with distilled water using a blue filter. The microammeter readings were plotted against milligrams of glucose on semilogarithmic paper. This standard curve has been found to be unchanged after 5 months.

PREPARATION OF SAMPLES. An accurately weighed sample of green or quick-dried plant material was extracted with hot 80 per cent alcohol in the usual manner and the alcohol removed by evaporation on a steam bath. Accurately measured volumes of plant juices were heated in a boiling water bath in order to destroy enzymatic activity. The extract or plant juice must be clarified so as to be free of all coloring matter and must be water-clear. The method as outlined by Hassid (3) has been found entirely satisfactory by the present author.

PROCEDURE. A sample of plant extract or juice containing 5 to 35 mg. of reducing sugar was evaporated to about 10 cc. on a water bath, cooled, and treated with 5 cc. of a saturated solution of neutral lead acetate. The excess lead was removed by adding

TABLE I. EFFECT OF REAGENTS AND CLARIFICATION

Replication	10-Mg. Sample			20-Mg. Sample			30-Mg. Sample		
	1	2	3	1	2	3	1	2	3
Colorimeter reading	48.1	48.0	48.0	53.5	53.7	53.5	60.7	60.8	60.8
	48.0	48.0	48.0	53.5	53.5	53.7	60.8	60.8	60.5
Glucose recovered, mg.	10.1	10.0	10.0	19.7	19.9	19.9	29.8	29.8	29.6
Glucose recovered, %	101	100	100	98.5	99.5	99.5	99.3	99.3	98.9



10 cc. of a saturated disodium phosphate solution. After the addition of about 0.3 gram of Norite decolorizing charcoal, the mixture was allowed to stand with frequent shaking for 30 minutes, and was then poured onto a Büchner funnel provided with a thin layer of talc as described by Hassid (3). The original container and funnel were washed several times with a small volume of distilled water and the filtrate was transferred to a 100- or 200-cc. volumetric flask. An aliquot of not more than 2 cc. containing 0.1 to 0.35 mg. of glucose was transferred to a 15-cc. centrifuge tube, diluted to 2 cc., and treated as described above for the standard glucose solutions. After the photoelectric colorimeter reading was obtained, the weight in milligrams of glucose in the aliquot was read directly from the calibration curve.

In order to determine total sugars, aliquots of 50 cc. of clarified extract were placed in 100-cc. volumetric flasks. The solutions were brought to the acid color of methyl red with dilute acetic acid. The quantity of acid necessary was determined on a separate 5- or 10-cc. aliquot. Two to four drops of a 1 per cent solution of Wallerstein invertase scales were added and the solutions allowed to stand overnight at room temperature. A blank on the invertase solution was run simultaneously. The flasks were then diluted to volume and aliquots taken for the determination of reducing sugars as described above.

### Experimental Results

In order to determine whether there were any loss during clarification and any interference by the reagents, solutions containing 10, 20, and 30 mg. of glucose were placed in three Erlenmeyer flasks and diluted to 10 cc. These were carried through the clarification process in triplicate and diluted to 200 cc., using 2-cc. aliquots for determinations. The results in Table I indicate no loss by clarification and no interference by the reagents used, and show a close agreement between replicate determinations over the range of the procedure.

Table II shows the effect of variations from the 2-cc. dilution and 5-minute heating time as called for in the procedure, using 0.15 mg. of glucose. These figures indicate a very slight increase in the amount of ferrocyanide formed when the dilution is reduced to 1 cc. No significant increase resulted in a longer heating period. This table also indicates that the colors are stable for at least 30 minutes but have increased after standing 2 hours.

Six plant materials were analyzed for reducing sugar and total sugar by the photocolometric and Quisumbing-Thomas methods. The results expressed as glucose are recorded in Table III. The photocolometric method gave values from 0 to 6.20 per cent higher than the volumetric method.

TABLE II. EFFECT OF VARIATIONS IN PROCEDURE

Variation from Procedure	Colorimeter Reading			Av.
No variation	50.5	50.5	50.7	50.6
Same as above after standing 30 minutes	50.5	50.5	50.5	50.5
Same as above after standing 2 hours	49.7	49.5	49.7	49.6
1-cc. dilution, heated 5 minutes	50.8	51.0	50.8	50.9
5-cc. dilution, heated 5 minutes	50.7	50.7	50.5	50.6
2-cc. dilution, heated 10 minutes	50.7	50.8	50.5	50.7

TABLE III. COMPARISON OF PHOTOCOLORIMETRIC WITH QUISUMBING-THOMAS METHOD

Material	Before Inversion			After Inversion		
	Glucose in Dry Material			Glucose in Dry Material		
	Colorimetric %	Volumetric %	Difference %	Colorimetric %	Volumetric %	Difference %
Dallis grass	2.74	2.58	6.20	7.54	7.35	2.58
Cabbage	39.3	37.9	3.69	39.6	37.4	5.88
Peas	0.89	0.89	0.00	22.8	22.5	1.33
Corn leaves	2.34	2.31	1.30	2.81	2.70	4.07
Celery	2.31	2.22	4.05	2.35	2.30	2.17
Orange juice <sup>a</sup>	3.60	3.58	0.56	7.60	7.44	2.15

<sup>a</sup> Recorded as per cent of glucose in original juice.

TABLE IV. RECOVERY OF PURE GLUCOSE ADDED TO 1 GRAM OF DALLIS GRASS

Initial Glucose Content Mg.	Glucose Added Mg.	Glucose Found Mg.	Glucose Recovered	
			Mg.	%
18.1	10	28.2	10.1	101
18.1	10	28.0	9.9	99
24.0	10	33.8	9.8	98
24.0	10	34.0	10.0	100
24.0	10	33.8	9.8	98

TABLE V. RECOVERY OF PURE SUCROSE ADDED TO 1 GRAM OF DALLIS GRASS

Initial Sucrose Content Mg.	Sucrose Added Mg.	Sucrose Found Mg.	Sucrose Recovered	
			Mg.	%
19.0	90	108.7	89.7	99.7
19.0	90	107.1	88.1	97.9
38.8	20	58.4	19.6	98.0
38.8	20	59.0	20.2	101.0
38.8	20	58.6	19.8	99.0

Several determinations by the photocolometric method were carried out in order to ascertain the recovery of added glucose and sucrose from 1-gram samples of Dallis grass. These results are recorded in Tables IV and V. All reducing values are recorded as glucose. The sucrose was hydrolyzed and determined along with the glucose as total sugar. The sucrose recovery was calculated from the total sugar and reducing sugar by using the factor 0.97 (2). There was good recovery of both glucose and sucrose.

This method has also been used successfully for the determination of starch and hemi-cellulose in plant materials, the starch or hemi-cellulose being hydrolyzed to reducing sugars and treated as described in the procedure for sugars.

### Summary

A rapid and accurate photocolometric method for the determination of sugars in plant materials is described. The procedure is simple and only one standard solution is required. The clarification process and reagents do not influence the color as read in the colorimeter. Slight variations in the procedure cause no appreciable differences in the results.

Results obtained on plant extracts and fruit juice by the photocolometric method compare favorably with those obtained by the Quisumbing-Thomas method, the results being from 0 to 6.20 per cent higher by the former. The method gives good recovery of glucose and sucrose added to plant material.

### Acknowledgment

The author wishes to thank J. R. Neller for his helpful suggestions and advice on this work.

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# A Rapid Potentiometric Method for Determination of Sulfate

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WITH the recent applications of vacuum-tube technic to potentiometric work, a number of new devices have been developed for analytical work. These setups are particularly suited for routine control, in that they are rapid, compact, and easy to operate. Such instruments as the electron beam spectrometer can be operated under conditions in which the change in potential may be as small as 50 millivolts. The use of this technic, being limited to those reactions which can be determined electrometrically, has stimulated considerable research for new indicator electrodes and potentiometric methods. It is apparent that any means by which such common ions as sulfate, nitrate, sulfite, etc., could be estimated electrometrically would greatly enhance the usefulness of these instruments.

Because of the great need (especially in control work) for a rapid method of determining sulfate ion, the electrometric possibilities of solving this problem were studied. As far as the authors were able to ascertain from the literature, there were no satisfactory methods for such a determination (1). Muller and Wertheim (3) describe an indirect method using the ferri-ferrocyanide system, but this, according to Kolthoff, is not convenient for practical use (2).

Preliminary experiments on the precipitation of the sulfate ion in the presence of such ions as persulfate had indicated that there was a slight change in the electrode potential at the equivalence point. This striking behavior seemed worthy of further investigation. Since barium persulfate is fairly soluble, attempts were made to adapt the persulfate ion to an electrometric determination of the sulfate ion.

## Experimental

The usual apparatus used in the classical method of potentiometric titrations was employed in this work. A shiny platinum electrode was used in conjunction with a calomel half cell.

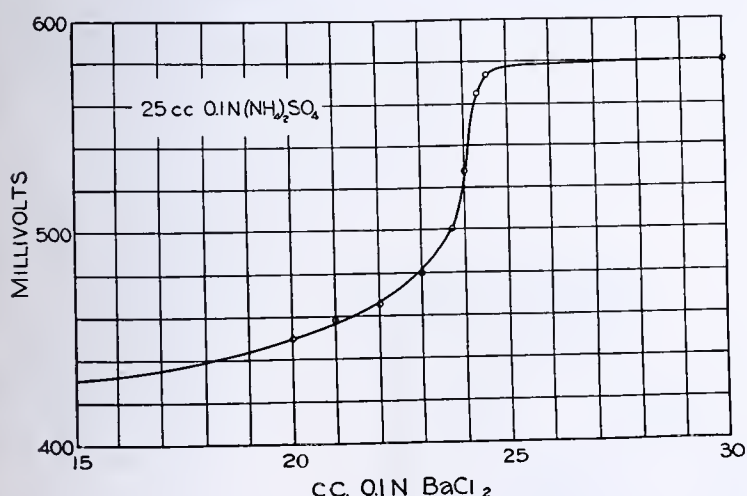


FIGURE 1

Initial experiments were carried out in an aqueous medium, using 0.1 N solutions. To 25 ml. of the sulfate solution a trace of persulfate was added and this in turn was titrated with 0.1 N barium chloride. The procedure was analogous to that

employed when using a ferri-ferrocyanide electrode. These preliminary experiments indicated that the break at the end point of the reaction, though definite, was neither large nor very sharp. In Figure 1 is shown a typical titration curve.

One of the factors which appeared to affect the magnitude of the break at the end point was the quantity of persulfate present. The best results were obtained when the amount of persulfate used was small (1 mg. or less). When larger charges of persulfate were employed, the break did not appear to be quite so sharp.

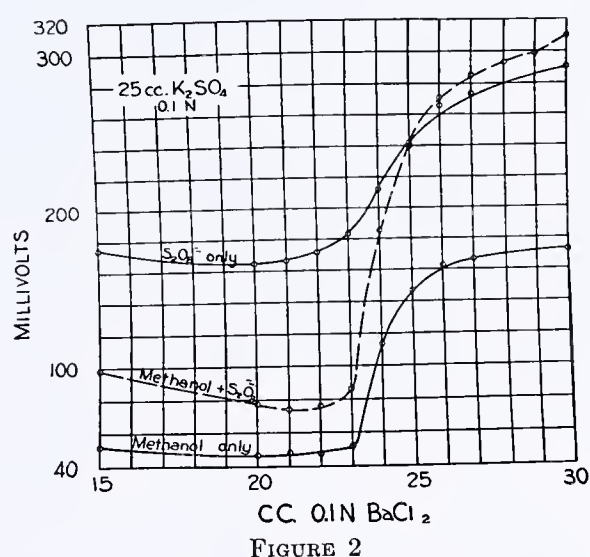


FIGURE 2

Once having established the fact that a change of electrode potential did occur in the vicinity of the stoichiometrical equivalence point, experiments to determine the effect of other factors were instituted. It was evident that a sharper break at the end point than shown in the preliminary tests would be desirable if this behavior was to be adapted to analytical purposes.

## Effect of Solvents

It is well known that the addition of alcohol has a stabilizing effect on many electrode potentials. In the attempt to improve the character of the sulfate titration curves, experiments were conducted using aqueous solutions of acetone, ethanol, and methanol. Although all three solvents gave better results, the behavior of methanol solutions was particularly striking in that a relatively large break was observed, while the potential (in the vicinity of the end point) came to equilibrium in a few minutes. Further experimentation established the fact that a break at the end point could be obtained when methanol was used in the absence of persulfate. It appeared that the effect of alcohol was additive to that of persulfate, resulting in a much larger break when both were employed simultaneously (Figure 2).

The best results with alcohol were obtained when the initial concentration of the methanol was in the range of 25 to 60 per cent. The sulfate concentrations which gave the best results were within the limits of 0.05 to 0.25 N. In the more dilute solutions the break was too small for analytical pur-



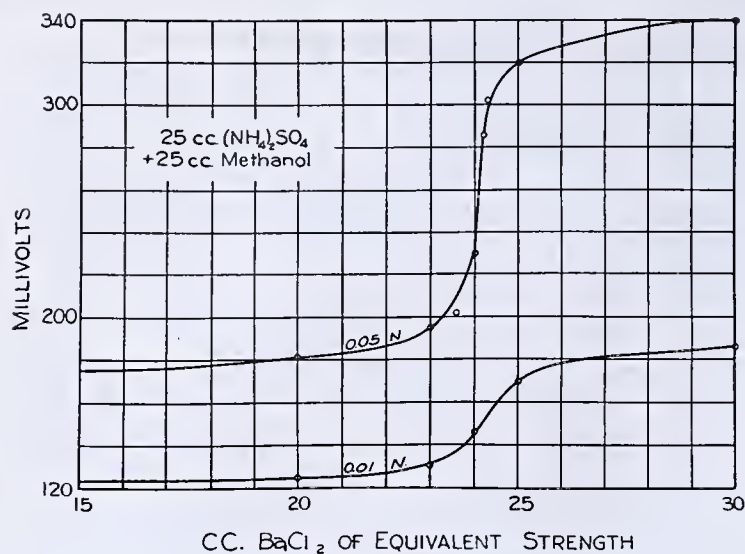


FIGURE 3

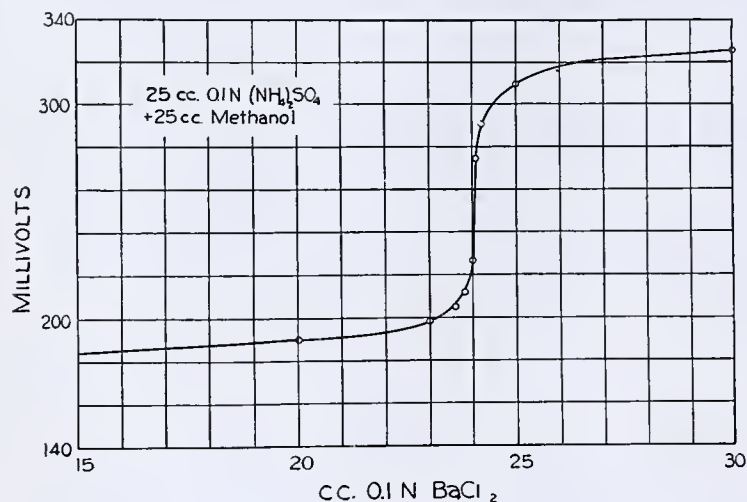


FIGURE 4

poses. These data are given graphically in Figure 3. When the concentration exceeded 0.25 *N* the precipitation was too heavy to give best results.

Although the solutions were carefully prepared and the data were always reproducible, the end point as shown by the titration curves did not occur at the stoichiometrical equivalence point but at that point where approximately 95 per cent of the sulfate had been precipitated (Figure 4). The authors were unable to account for this behavior.

Since the potential even in alcoholic solutions had a tendency to drift, the procedure for carrying out the titration was

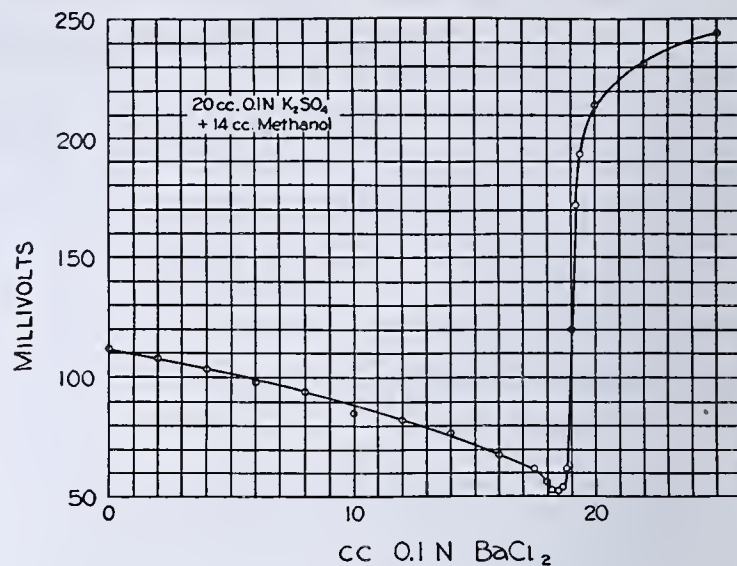


FIGURE 5

standardized as follows: The titration was carried out in the usual manner except in the matter of time. Instead of waiting for equilibrium, the e. m. f. was immediately determined and a minute later it was redetermined. In no case were more than 2 minutes allowed to elapse between each addition of barium chloride. Although the curves (obtained by plotting the potential after equal time intervals) were not as regular, considerable time was saved and the same results were attained in the end (Figure 5).

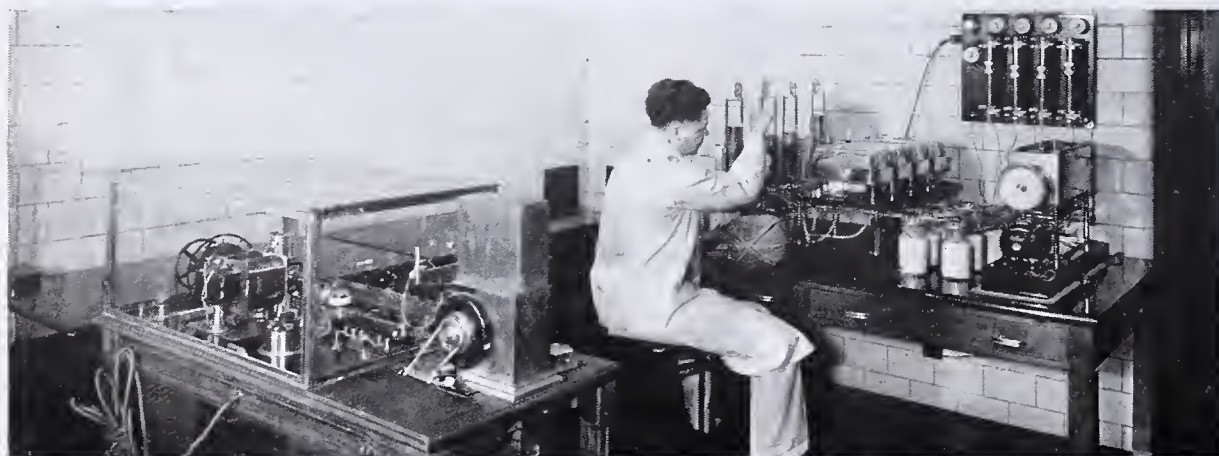
### Interfering Ions

In order to determine other limitations of this method, the effect of foreign ions on the potential was studied. The presence of sulfite, sulfide, and thiosulfate ions completely eliminates the break in potential at the equivalence point. However, this should not detract from the value of the procedure, since these ions can readily be eliminated from solution. The chloride and nitrate ions have no apparent effect on the titration curve other than to alter slightly the position of the maximum  $\Delta E / \Delta c$ . Very poor results are also obtained when the titration is performed in distinctly acid or basic solutions.

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The oxygen consumption of four small laboratory animals can be determined simultaneously on the Benedict metabolism apparatus (right), reading directly on the four small gasometers in front of the operator. Electrocardiograph in the left foreground.

Courtesy, Lilly Research Laboratories



# An Aspiration Method in Determining Ammonia and Other Volatile Gases

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**A**SPIRATION methods have been described for the micro-determination of ammonia and other volatile gases, but they appear not to have been adopted widely by the profession as a whole. This is the more surprising in view of the considerable advantages of aspiration over straight distillation, and the well-known disagreeable tendency of the latter to give trouble by bumping.

A step in the right direction has been made by Green (1) who has proposed distillation and agitation by steam. In this method the steam has a triple function: it heats, it prevents bumping by stirring, and it sweeps out the escaping gases. While steam is available at some points in most laboratories, yet there are times and places where it is not convenient to use it. For instance, the author wished to include the determination of nitrogen as part of the regular laboratory work in large classes, and it was out of the question to set up a sufficient number of stills, since steam was not piped to the desks in the analytical laboratory. However, suction was available, and it was found possible to determine nitrogen very quickly, simply, and accurately by aspiration.

The sample may be contained in either a Kjeldahl or an Erlenmeyer flask, fitted with a thistle tube which reaches the bottom and an outlet tube leading to a petticoat bubbler in an absorption bottle, preferably of tall narrow form; an outlet tube from the latter leads directly to the suction line. It was determined by experiment that no entrainment of the reagents occurred from either of the flasks, even with vigorous

aspiration; at the same time the absorption of the ammonia, or other gas, is complete when an efficient bubbler is used.

The gas may be liberated by addition of the reagent through the thistle tube while aspiration is in progress, with no danger of loss. Some heat must be applied, since quantitative removal of the gas is very slow at room temperature; it may be supplied by direct heating or by a water bath. The process is complete in from 10 to 30 minutes, depending upon the volume and the rapidity of heating. In the case of ammonia, the gas may be absorbed in a small excess of standard acid, and titrated with standard base, using methyl red as indicator. The aspiration method has a further advantage over straight distillation in that little dilution of the absorbent occurs. No water-cooled condenser is necessary, although one may be used if desired. Only a small excess of the liberating agent need be used and, since there is no bumping, practically no attention is required.

The time necessary for the complete removal of ammonia depends upon the rapidity of heating. Small volumes and rapid heating are of advantage where speed is important; on the other hand, a water or steam bath is to be preferred where it is desired to run a series of analyses with a minimum of attention.

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RECEIVED April 27, 1938.

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# Direct Determination of Iron in Malt Beverages

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**I**T IS KNOWN that relatively small amounts of iron impair the colloidal stability of beer and cause development of abnormal tastes and off colors. The extent to which traces of iron, as well as other metallic elements, may function as oxidation catalysts has been under consideration in the authors' laboratories for some time and is receiving special study. There is obviously a need for a rapid and, at the same time, adequately accurate procedure for carrying out iron determinations on beer, both as an aid in research work in these directions and as a means of regularly scheduled control.

Normally, traces of iron are present in practically all beers. Iron which may occur in water and brewing materials, if not filtered out with the spent grains in the mash tub, appears to be very largely eliminated with the coagulum which forms during kettle operations. Nevertheless, traces remain and may be augmented by subsequent contact with iron surfaces. The amounts of iron found are usually 0.5 part per million or less. Yet amounts even slightly in excess of this concentration have been known to result in the development of a bitter taste, gradual acquisition of a dark color, loss of brilliance, and chill-haze development. It is also believed that, as a result of its catalytic influence on oxidation, the shelf life of packaged beer is definitely shortened.

Usual procedures for determining iron in beer, based on

classical methods, call for a rather lengthy, involved treatment to reduce the sample to a form suitable for analysis. Methods generally applicable may be found in reference books (4, 6, 7).

Siebenberg and Hubbard (5) adapted the ferrocyanide method for use in beers. This method calls for evaporating and ashing, dissolving the ash in hydrochloric acid, precipitating copper, lead, and tin with hydrogen sulfide, removing hydrogen sulfide, oxidizing the iron, a phosphate separation to separate the iron from any nickel, and finally dissolving the iron-containing precipitate and determining the iron colorimetrically with ferrocyanide solution. Aside from the length of time involved, it is evident that opportunity for loss or contamination, representing unknown sources of error, may be presented by the number of manipulations involved in such a procedure.

In the method as developed by the authors, it has been found possible to determine the iron in beer quickly and directly without having to ash the beer or to subject it to any other preliminary treatment. In contrast with the considerable time required for existing methods, results are obtainable within 45 minutes.

The reagent utilized in this procedure is 2,2'-bipyridine ( $\alpha, \alpha'$ -dipyridyl). Hill (2) investigated and described its use for the determination of iron and reported on its applicability



for determining iron in various biological materials. While Bode (1) investigated the use of this reagent for determining iron in beer, his method requires a lengthy digestion with sulfuric acid and hydrogen peroxide for the purpose of destroying organic matter and hence offers no advantage over the other methods described. Hill's paper may be referred to for a bibliography of methods for preparing the reagent. However, 2,2'-bipyridine is now available through regular chemical supply houses, so that the need for the tedious preparation and purification of this compound is eliminated.

TABLE I. EFFECT OF SODIUM HYDROSULFITE

Iron Added P. p. m.	Iron Found	
	On reduction with sodium hydrosulfite P. p. m.	Without sodium hydrosulfite P. p. m.
None	0.1	0.1
1.0	1.1	1.1
2.0	2.1	2.1
3.0	3.1	3.0
4.0	...	4.2

This reagent reacts with ferrous iron to give an intense red coloration. Ferric iron does not give this color and it is usually necessary, in employing this reagent, to reduce the iron to the ferrous state before applying the test. Hill originally used iron-free sodium hydrosulfite for this purpose. Recently, Kohler, Elvehjem, and Hart (3) suggested the use of hydroquinone, as easier to purify and superior to hydrosulfite as a reducing agent for the purpose. However, the authors' work shows that iron in beer exists in the ferrous condition, and that no preliminary reduction is necessary in carrying out routine tests by this procedure. Within the limits of error of visual matching, the intensity of color is found to be the same whether reduction with hydrosulfite has or has not been employed (Table I).

For the amounts of iron usually encountered in beer, the color intensity of the test solutions ranges between a faint orange and a deep reddish orange. The orange shade is due to a mixture of the yellow color of the beer itself with the red color of the iron complex.

TABLE II. ANALYSIS OF BEERS

Sample	Iron Added P. p. m.	Iron Found		
		2,2'-Bipyridine method P. p. m.	Siebenberg- Hubbard ferrocyanide method P. p. m.	Thio- cyanate <sup>a</sup> method P. p. m.
A	None	0.5	0.5	...
A	1.0	1.5	1.4	...
A	3.0	3.5	4.0	...
A	5.0	5.0	5.6	...
B	None	2.5	2.2	...
C	None	1.8	1.5	...
D	None	1.9	1.9	...
E	None	1.7	2.0	...
F	None	1.4	1.5	...
G	None	0.5	...	0.4
H	None	2.5	...	2.5
I	None	3.5	...	3.4
J	None	1.5	...	1.3

<sup>a</sup> This method is widely used and consists in evaporating and ashing the beer, taking up with hydrochloric acid, heating to hydrolyze any pyrophosphates, oxidizing with  $\text{KMnO}_4$ , and then adding thiocyanate.

The method has been worked out for practical use and requires no special photometers or other complicated color-matching equipment. Results are generally satisfactory for ordinary control work. However, for work requiring a higher degree of precision than that offered by simple visual matching of color, the method may be easily adapted to the more precise visual or photoelectric photometers. In matching the colors of the sample with standards, use is made of the Walpole effect whereby the tube containing the standard is viewed through a tube containing untreated sample in order to compensate for the beer color. A simple block comparator is used, similar to those used for colorimetric pH determinations.

## Method

**APPARATUS REQUIRED.** Uniform test tubes graduated at 10 ml. and a block comparator with six holes. The tubes and comparator are similar to those commonly used in pH work.

**REAGENT.** To 100 mg. of 2,2'-bipyridine add 2 ml. of acetic acid (1 + 2). Stir and dilute to 50 ml. with distilled water.

**STANDARD IRON SOLUTION.** Weigh out 3.512 grams of ferrous ammonium sulfate hexahydrate (Mohr's salt), dissolve in distilled water, add 2 drops of hydrochloric acid, and dilute to 500 ml. with water. Dilute 10 ml. of this solution to 1 liter. This final diluted solution contains 0.01 mg. of iron per ml. One milliliter of this solution in 10 ml. is equivalent to one part per million of iron. This solution is used to prepare the permanent standards and should be made fresh before use.

**SODIUM HYDROSULFITE SOLUTION.** Prepare immediately before use a small quantity of an approximately 2 per cent solution from iron-free sodium hydrosulfite.

**PREPARATION OF PERMANENT STANDARDS.** Pipet the desired quantity of standard iron solution into the test tube, add 0.5 ml. of the sodium hydrosulfite solution, and make volume to 10 ml. with distilled water. Add 0.5 ml. of the reagent and mix. Cork the test tube and seal with paraffin. A convenient series of standards for beer may be prepared to contain 0.00 to 0.05 mg. of iron in steps of 0.005 mg. (0 to 5 parts per million in steps of 0.5 part per million). These standards will keep for months in the dark.

**METHOD.** Place 10 ml. of degassed beer in each of three test tubes. Add 0.5 ml. of the 2,2'-bipyridine reagent to one of the tubes and mix. Heat in a water bath at 70° C. for 30 minutes to develop the color. At the end of this time, compare the color with the permanent iron standards in the block comparator, arranging the tubes as shown in Figure 1.

## Accuracy and Recovery

A beer of low iron content was selected and small amounts of iron, as indicated in Table II, were added. The resulting beers were then analyzed by the above method and also by the procedure of Siebenberg and Hubbard with the excellent recovery noted. In Table II also appear results by the thiocyanate method, showing the agreement to be expected with the existing procedures.

## Possible Interferences

In order to check up on the extent to which small amounts of other metallic elements would be capable of interfering with the accuracy of the procedure, three beers were prepared containing, respectively, 1, 3, and 5 parts per million of iron. Each was divided into separate portions and to each portion were then added 5 parts per million of aluminum, chromium, cobalt, copper, lead, manganese, nickel, tin, and zinc. One hundred per cent recovery was observed in all cases within experimental error.

Since the amounts of the different metals used in this test far exceed amounts which are normally to be encountered, the procedure is demonstrated to be entirely satisfactory from the standpoint of possible interferences under usual conditions.

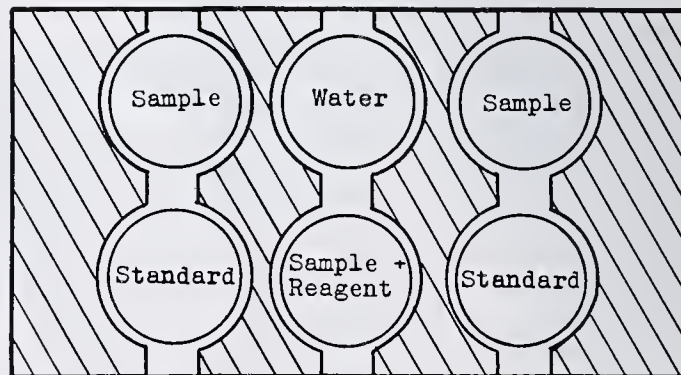


FIGURE 1. CROSS SECTION OF BLOCK COMPARATOR SHOWING ARRANGEMENT OF TUBES



In connection with studies which resulted in the development of this method, tests were also carried out on the applicability of other iron reagents and included 1,10-phenanthroline. This is an oxidation-reduction indicator, forming a colored iron complex, and is structurally similar to 2,2'-bipyridine. The results obtainable were similar to those found for 2,2'-bipyridine, though 2,2'-bipyridine is to be preferred. The color with 1,10-phenanthroline tends toward the orange rather than the red, making visual comparisons much less sensitive than with the 2,2'-bipyridine. Moreover, this reagent was more susceptible to interferences by traces of certain metals, particularly cobalt, nickel, and copper.

Over a period of more than 3 years, many hundreds of samples of beer, ales, and the like have been subjected to the above iron test in the authors' laboratories, with entirely satisfactory results. It has the special advantage, by reason of the rapidity with which results may be secured, that the iron content of beer in process, during storage, and in the

finished form, may be regularly and carefully controlled. Such regular control is impracticable with the more time-consuming methods. By means of such regularity of control, it has been possible to discern danger signals far ahead of actual trouble and to take necessary remedial steps.

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## A Precise Method for the Determination of Carotene in Forage

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A REPORT of recent methods for the determination of carotene in forage is given by Munsey (2) and his referees. These methods give consistent results only when special precaution is taken. The Guilbert method (1) has been used in this laboratory for some time, but the use of ethyl ether in the extraction of the carotene from the saponified mixture is objectionable. Peterson and Hughes' (3) modification of Guilbert's method eliminates the use of ethyl ether and extracts the carotene directly from the saponified mixture with petroleum ether, forming emulsions which result in a loss of carotene.

During the past year a modification of this method (1, 3) has been used in the authors' laboratory; it permits the use of definite quantities of reagents, avoids the formation of emulsions, and gives more precise results.

### Procedure

Reflux a 5- to 10-gram sample 40 minutes with 200 cc. of ethyl alcohol (approximately 95 to 97 per cent). Filter the hot alcoholic solution through a No. 31 Whatman paper placed in a Büchner funnel, and wash the residue with hot ethyl alcohol until the alcoholic filtrate comes through clear (150 cc. of hot alcohol are usually sufficient). Make the alcoholic filtrate up to 400-cc. volume, transfer one-half to a 250-cc. volumetric flask, and add 25 cc. of 10 per cent alcoholic potash. Shake and let the alkaline alcohol solution stand for 2 hours at room temperature to ensure complete saponification, or place the flask containing the alkaline alcohol solution in hot water for 0.5 hour at 80° C. to hasten saponification; cool and make up to volume. Transfer 25 cc. of the saponified alcoholic carotene solution to a 100-cc. separatory funnel. Add 15 cc. of petroleum ether (b. p. 40-60°) and shake the alcohol and petroleum ether vigorously. Add 7 cc. of water to the contents in the separatory funnel and again shake vigorously. Drain off the alcoholic solution into a similar separatory funnel and extract twice more with 10 cc. of petroleum ether. The last extraction of the petroleum ether will be colored.

Tests have shown that the carotene is almost completely removed with the first extraction of petroleum ether. Combine the petroleum ether extracts and wash gently with 25-cc. portions of distilled water until the wash water no longer gives a color with phenolphthalein. Extract the xanthophyll from the

petroleum ether solution with 25-cc. portions of 85 per cent methyl alcohol until the alcohol is colorless. For the first extraction with 85 per cent methyl alcohol, pour the alcohol gently down the sides of the separatory funnel so as not to disturb the small amount of water left in the bottom of the separatory funnel. Drain off approximately 5 cc. of the alcohol and water and then shake the remaining alcohol and petroleum ether gently. Subsequent extractions with 25 cc. of 85 per cent methyl alcohol can be shaken more vigorously without danger of forming emulsions. Finally, extract once or twice more with 25 cc. of 90 per cent methyl alcohol. Filter the petroleum ether-carotene solution through anhydrous sodium sulfate, which is placed over a cotton plug in the stem of a funnel, into a 50-cc. volumetric flask, and make up to volume with petroleum ether. Compare the carotene solution against the standard dye solution as described by Guilbert (1) or determine the carotene spectrophotometrically.

Smaller quantities of alcohol can be used for the extraction of carotene from the forage if the size of the sample is decreased. Reflux a 1- to 2-gram sample with 50 cc. of alcohol, filter, and wash the residue with small portions of hot alcohol through a No. 3 fritted-glass crucible directly into a 100-cc. volumetric flask containing 5 cc. of 20 per cent potassium hydroxide-alcohol solution under a bell jar. Proceed as described above.

### Results and Discussion

Determinations of carotene on commercial dehydrated alfalfa meal by Guilbert's method and the modified method are shown in Table I. More carotene is recovered by the modified method. The difference of the two methods may be due to the loss of carotene during the evaporation of the ethyl ether from the carotene. Results of duplicate analyses of

TABLE I. DETERMINATION OF CAROTENE IN DEHYDRATED ALFALFA BY THE GUILBERT AND MODIFIED METHODS

Sample No.	Guilbert Method Mg./100 g.	Modified Method Mg./100 g.
1	7.6	8.3
2	7.8	8.6
3	16.0	16.5
4	6.7	8.1
5	7.1	8.5



carotene in dehydrated alfalfa with a carotene content of 10 to 20 mg. per 100 grams are reproducible within 0.1 mg. per 100 grams when the carotene content is determined photoelectric-spectrophotometrically, using Peterson and Hughes' (3) extinction coefficient for  $\beta$ -carotene.

To determine whether the extraction of carotene was complete with 95 per cent alcohol, the residue from the alcoholic extract was analyzed for carotene by the Guilbert and Peterson-Hughes methods. No measurable amount of carotene was found in the residue.

The use of 95 per cent alcohol permits rapid filtering, washing of the alcohol-carotene solution from the forage residue, and the use of definite quantities of reagents in the extraction of carotene. To prevent the formation of emulsions and to obtain a quantitative extraction of the carotene

from the alkaline alcohol solution with petroleum ether, it is important that the concentration of the alcohol be between 70 and 75 per cent. At this concentration the separation of the petroleum ether from the water and alcohol phase is clear cut.

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# Determination of Organic Sulfur in Gas

## Titration of Sulfate in the Sulfur Lamp with Barium Chloride Using Tetrahydroxyquinone as an Indicator

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AN ADAPTATION of the A. S. T. M. (1) method for the determination of sulfur in motor fuels, with which it is possible to determine the concentration of organic sulfur in gas, has been described (3). The speed and convenience of this method, as well as its accuracy, have proved of great value, and it is now extensively used.

In this procedure, the gas is burned, and the sulfur dioxide formed by the combustion of sulfur compounds in the gas is absorbed in standard sodium carbonate solution. The excess sodium carbonate is titrated with standard hydrochloric acid, and the sulfur concentration is calculated from the amount of carbonate used and the volume of gas burned. Thus, the sulfur is determined through the acidic character of the sulfur dioxide formed.

In some cases this has been found objectionable, since any other constituent of an acid character absorbed by the carbonate will be determined as sulfur, and the result will be too high. The sulfur can be determined gravimetrically as barium sulfate, but at a sacrifice in time and convenience.

The present paper describes an adaptation of a procedure for the direct titration of sulfates with barium chloride which may be used in conjunction with the sulfur lamp method (3). Titration of sulfates with standard barium chloride solution using tetrahydroxyquinone as an indicator has been discussed by Sheen and Kahler (2). Such a procedure will overcome the objection noted to the acidimetric titration which has been used heretofore with the sulfur lamp, yet retain the speed and convenience of the sulfur lamp and volumetric determinations. The accuracy obtainable by the barium chloride titration has been tested, and the results of the experiments are presented here. While the discussion is confined to the determination of organic sulfur in gas, obvious changes in apparatus will make the procedure applicable to the determination of sulfur in motor fuels (1) with an accuracy comparable to that shown for gas.

### Materials and Reagents

Standard barium chloride solution, 1 ml.  $\approx$  1 mg. of sulfur (7.634 grams of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  per liter). Standardize gravimetrically by precipitation as barium sulfate.

Sodium carbonate solution, containing 3.306 grams of the anhydrous salt per liter.

Hydrochloric acid, containing 2.275 grams of hydrochloric acid per liter. This and the sodium carbonate solution are the same as used in the acidimetric determination of organic sulfur. It is convenient to use the strength noted, although exact standardization is not necessary.

Methyl orange indicator solution.

Tetrahydroxyquinone indicator (THQ, obtained from the W. H. & L. D. Betz Laboratories, Philadelphia, Pa.).

Ethyl alcohol, ethyl alcohol denatured by formula 30 or 3-A, or isopropyl alcohol.

### Procedure

For the determination of organic sulfur in gas the following procedure is now proposed.

The metered gas is burned at a rate from 14 to 28 liters (0.5 to 1 cubic foot) per hour, and the products of combustion are absorbed in sodium carbonate solution in the A. S. T. M. sulfur lamp (1, 3). At the conclusion of the test, the lamp is washed down with the smallest possible quantity of distilled water, and 3 drops of methyl orange indicator are added. The solution is neutralized with dilute hydrochloric acid which, if standardized, will give an estimate of the sulfur present. At this point the determination was concluded according to the earlier procedure.

The tan color of the acid methyl orange is discharged with a few drops of the sodium carbonate solution, and 30 ml. of ethyl or isopropyl alcohol are added (2). About 0.22 gram of tetrahydroxyquinone indicator is added, and the solution is mixed well and titrated with standard barium chloride solution. The end point is reached when the color of the solution changes from yellow to red, which is permanent with good mixing.

### Calculation of Results

From the total volume of barium chloride used, 0.05 ml. is subtracted for a blank. Concentration of organic sulfur in the gas is then calculated using the following expression:



$$\frac{\text{Ml. of BaCl}_2 \times \text{strength of BaCl}_2 \text{ (in mg. of S per ml.)}}{\text{Cubic feet of gas burned (corrected to N. T. P.)}} \times 1.543 =$$
$$\text{S concentration in gas in grains per 100 cubic feet}$$

Discussion

In the development of the method, several points required examination. First, it has been reported (2) that the CO<sub>3</sub>--ion interferes with the determination of sulfate by titration with barium chloride. The excess sodium carbonate in the absorbing solution must, therefore, be completely neutralized. It was proved experimentally that correct results were obtained only when neutralization of the excess carbonate was carried to the methyl orange end point. Neutralization of the solution containing sulfate to the phenolphthalein end point as described by Sheen and Kahler (2) is not sufficient when sodium carbonate is used as the absorbing solution. To keep the red-dish color of methyl orange in acid solution from interfering with the red barium chloride-tetrahydroxyquinone end point, it is just discharged with 3 or 4 drops of sodium carbonate solution. Since barium chloride is neutral, there is no increase in acidity of the solution to bring back the red methyl orange color; moreover, the addition of the alcohol has a favorable effect in reducing the intensity of the methyl orange color. Numerous experiments have proved that the presence of the methyl orange offers no difficulty in recognizing the red barium chloride-tetrahydroxyquinone color.

It was desirable to perform the whole determination in the sulfur lamp absorber without intermediate transfer of the solution to other vessels. The volumes of solution usually employed in sulfur lamp determinations are larger than the 25 ml. recommended by Sheen and Kahler (2), and are variable because of the necessity of washing down the lamp. An effort should be made to keep the volume at a minimum, however, and it seldom need exceed 35 to 40 ml. Under these conditions, 30 ml. of alcohol have been found adequate. Absolute ethyl alcohol and isopropyl alcohol have been found to be interchangeable. It is preferable, because of the larger volume, to add about 0.22 gram of the indicator. A blank of 0.05 ml. of the barium chloride solution was necessary to give a distinct end point, and this quantity should be subtracted from the total standard solution used in a determination.

The red color obtained at the end point was very distinct, and easier to detect than the methyl orange end point in acidimetry.

In a series of preliminary tests of the procedure, sulfur was added to the sodium carbonate absorbing solution as standard sulfuric acid, instead of burning gas containing sulfur compounds. The quantity of acid added was determined acidimetrically by titrating the excess sodium carbonate with standard hydrochloric acid solution and methyl orange indicator, and the sulfate was determined by titration with standard barium chloride solution and tetrahydroxyquinone indicator. The solutions used were of the following strengths:

H<sub>2</sub>SO<sub>4</sub>: 1 ml. ≈ 0.507 mg. of S (gravimetric standardization)  
Na<sub>2</sub>CO<sub>3</sub>: 1 ml. ≈ 0.994 mg. of S (standardized independently)  
BaCl<sub>2</sub>: 1 ml. ≈ 1.0026 mg. of S (gravimetric standardization)

The experiments were performed in a sulfur lamp absorber according to the procedure outlined above, with the results shown in Table I.

TABLE I. COMPARISON OF ACIDIMETRIC AND BARIUM CHLORIDE-TETRAHYDROXYQUINONE TITRATIONS OF SULFATE SOLUTIONS

H <sub>2</sub> SO <sub>4</sub> Taken Ml.	≈S Taken Mg.	Na <sub>2</sub> CO <sub>3</sub> Used Ml.	≈S Found Mg.	Differ- ence Mg.	BaCl <sub>2</sub> Used Ml.	≈S Found Mg.	Differ- ence Mg.
16.00	8.11	8.20	8.14	0.03	8.05	8.02	0.09
10.00	5.07	5.10	5.07	0.00	5.10	5.06	0.01
5.20	2.63	2.61	2.59	0.04	2.60	2.56	0.07
4.00	2.00	2.04	2.03	0.03	2.10	2.06	0.06
			Av.	±0.025			±0.06

From these data, it appears that the barium chloride-tetrahydroxyquinone titration gives results of ample accuracy. The average error of 0.06 mg. of sulfur is of the same magnitude as that found by Sheen and Kahler (2) in the determination of sulfur in oil.

TABLE II. COMPARISON OF ORGANIC SULFUR CONCENTRATIONS IN GAS BY THREE PROCEDURES

Gas Sample	Sulfur Concentration		
	Acidimetrically Grains/100 cu. ft. <sup>a</sup>	By BaCl <sub>2</sub> -THQ Grains/100 cu. ft. <sup>a</sup>	Gravimetrically Grains/100 cu. ft. <sup>a</sup>
1	10.7	9.9	10.1
2	12.4	11.9	11.5
3	13.7	13.1	13.0
4	13.3	12.6	12.6
5	13.5	12.5	12.7
6	15.0	14.1	14.0

<sup>a</sup> 1 grain per 100 cu. ft. = 0.0229 gram per cu. m.

As a final check, determinations were made on several gas mixtures containing varying amounts of organic sulfur compounds. Two gas samples were collected simultaneously for each test in two calibrated gas holders. After combustion and absorption of the sulfur dioxide formed in sodium carbonate solution in separate sulfur lamps, the sulfur concentration was determined in each acidimetrically. Then the solution in one absorber was titrated with the standard barium chloride solution, while that in the other was subjected to gravimetric determination of sulfur by precipitation as barium sulfate. The standard sodium carbonate and barium chloride solutions were of the concentrations noted above. About 22.5 liters (0.8 cubic foot) of gas were burned for each separate determination. The concentrations of organic sulfur found in the gas in six tests are summarized in Table II.

Excellent agreement between the results of barium chloride-tetrahydroxyquinone and gravimetric determinations is observed. The accuracy obtainable by the volumetric procedure is well within the limits generally required in these determinations.

The acidimetric determinations on these gas samples gave results on the average 0.018 gram per cu. m. (0.8 grain per 100 cubic feet) too high. Nitrates were found in the absorption solution in quantities which may at least partially account for these differences. The source of the nitrates has not yet been determined.

Summary

The use of standard barium chloride solution for volumetric determination of sulfate with tetrahydroxyquinone indicator is adaptable to the procedure for the determination of the concentration of organic sulfur compounds in gas. Instead of determining the sulfates acidimetrically in the absorption solution contained in the A. S. T. M. sulfur lamp (3), the sulfate may be determined directly by titration with barium chloride solution. This modification avoids errors which may arise from the presence of other acidic constituents in the combustion products of the gas, which would be determined as sulfur by the acidimetric titration.

The accuracy of the method is such that the concentration of organic sulfur in gas can be determined to within ±0.0045 gram per cu. m. (±0.2 grain per 100 cubic feet) if approximately 28 liters (1 cubic foot) of gas are burned. This accuracy is as great or greater than that given by any other procedure so far described, and is attained at no sacrifice in speed or convenience.

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# A Colorimetric Method for the Determination of Ascorbic Acid

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DURING studies of the diazo reaction in urine (13, 14) it was observed that ascorbic acid reduces certain diazonium salts, but not the azo color formed upon coupling. This decrement in the concentration of the diazonium ion bears a direct relationship to the diminution in the coupling color. Standardization of this relationship affords a simple, accurate colorimetric method for the determination of vitamin C in various media.

To 5.0 cc. of sulfanilamide (5.00 mg. per cent), 1.0 cc. of sodium nitrite (0.050 per cent) and 1.0 cc. of sulfosalicylic acid (20.0 per cent) were added. The solution was allowed to stand 1 to 3 minutes and 1.0 cc. of urea (1.0 per cent) was added. After 5 minutes, 10.0 cc. of a fresh 10 per cent acetic acid solution containing varying concentrations (0.100 to 0.400 mg.) of the vitamin were added. After 5 minutes, 7.4 cc. of 1-dimethylnaphthylamine solution (1.0 cc. diluted to 500 cc. with 95 per cent alcohol) were added and the solution was mixed. After 10 minutes but within 50 minutes the colors developed were compared in a colorimeter with appropriate standards, prepared by diminishing the sulfanilamide concentration and replacing the vitamin solution by vitamin-free 10 per cent acetic acid.

In the standardization work, weighed samples of the crystalline vitamin (Merck & Co., Inc.) were dissolved in 10 per cent acetic acid, and aliquots were diluted to appropriate concentrations. These solutions were prepared fresh for each series of determinations. Fresh nitrite solutions were made up daily, although these solutions are stable for at least 2 to 3 days. Merck's reagent grade sulfosalicylic acid was used, although sulfuric acid appears to be equally satisfactory. The 1-dimethylnaphthylamine (Eastman No. 1063) satisfied Marshall's requirements (9) for the use of this reagent in diazotization procedures. Crystalline sulfanilic amide (Winthrop) was used to form the diazonium salt, and double-distilled water was used throughout the standardization work. The blank reagents contained no reducing substances as determined by the 2,6-dichlorophenolindophenol titration of Tillmans (16) as modified by Harris and Ray (5).

The variation from a strict inverse proportion of sulfanilamide concentration and column length was determined by comparing known solutions in distilled water differing by 100 per cent in sulfanilamide concentration. Each figure in column 3 of Table I represents the average of 9 separate determinations, five or more readings being taken in each determination. The colors produced by the coupling reaction matched excellently, and the average colorimetric readings were within  $\pm 0.1$  mm. This deviation is equivalent to 0.01, 0.02, and 0.05 mg. per cent sulfanilamide, the higher values being associated with the higher concentrations. These deviations are equivalent to errors of 0.8 to 1.0 per cent for readings differing by 10.0 mm.

TABLE I. COMPARATIVE DETERMINATIONS

Concentration of Standard Mg. %	Concentration of Unknown Mg. %	Concentration by Color Comparison Mg. %	Error ( $\pm 1$ ) for Readings Differing by 10 Mm. %
0.625	1.25	1.16 1.17	7
1.25	2.50	2.32 2.35 2.32	7
2.50	5.00	4.85 4.95	2

Under the conditions selected, vitamin concentrations of 0.100 mg. in the 10 cc. of 10 per cent acetic acid produced a color decrement of about 7 colorimeter units. At vitamin concentrations of 0.025 mg. no color decrement could be measured, and at 0.050 mg. the decrement was too small to

give consistent results. Values were established at intervals of 0.050 mg. of ascorbic acid over the range 0.100 to 0.400 mg. Each figure in column 2 of Table II is an average of 9 separate determinations, five or more readings being taken in each determination. Standards were prepared in the absence of ascorbic acid by diminishing the sulfanilamide concentration. All colors were matched within 1.0 to 4.0 mm. Thus, the errors due to variations from Beer's law are less than 4 per cent. The average in each series of determinations deviated by  $\pm 0.1$  to 0.2 mm., or  $\pm 0.01$  to 0.10 mg. per cent sulfanilamide prevented from coupling. The highest deviations in milligrams per cent can occur only at the highest concentrations reduced.

TABLE II. SULFANILAMIDE REDUCED

Weight of Vitamin Mg./10 cc.	Sulfanilamide Reduced		
	Mg. %	Mg.	Molecules
0.100	1.74	0.087	1.15
	1.68	0.084	1.19
	1.67	0.084	1.19
0.150	2.24	0.112	1.34
	2.16	0.108	1.39
0.200	2.63	0.132	1.51
	2.73	0.137	1.46
	2.75	0.138	1.45
	2.76	0.138	1.45
0.250	2.91	0.146	1.71
	2.92	0.146	1.71
	2.93	0.147	1.70
	2.94	0.147	1.70
	2.95	0.148	1.69
0.300	3.27	0.164	1.83
	3.49	0.175	1.71
	3.57	0.179	1.67
	3.60	0.180	1.67
0.350	3.88	0.194	1.80
0.400	4.11	0.206	1.94
	4.13	0.207	1.93
	4.17	0.209	1.91

At concentrations of the vitamin above 0.4 mg., with an initial 10 mg. per cent sulfanilamide, the reduction of the diazonium salt is accompanied by the formation of a yellow color which makes colorimetric comparison difficult. (The formation of this color is discussed below.) The calibration curve of Figure 1 is accordingly restricted to that range of concentrations lying between 0.1 and 0.4 mg., or 0.01 and 0.04 mg. of the vitamin per cubic centimeter of unknown.

The change in slope below 1 mg. per cent of vitamin indicates an exponential graph. Over the desired range, however, the data may be plotted within the experimental error as a straight line described by the simple slope intercept expression  $Y = 0.8 X + 1$ . For a series of determinations this line may be plotted and the value read directly, or more simply, a two-line nomograph may be constructed.

It has been shown that nitrites are reduced (6) to hydroxylamine (8) by ascorbic acid. In the present procedure it is not possible to test for an excess of the nitrite ion by the usual starch-iodide procedure, since the diazonium salt oxidizes the iodide. To lower the effect of possible nitrite oxidation of the vitamin, an excess of urea was added, and the reaction mixture was permitted to stand for 5 minutes. Any nitrite oxidation of the vitamin should produce a trend opposite to that observed (Table II, column 4). Experiments, run in duplicate at increasing vitamin concentrations with and without the urea treatment, showed no differences at concentrations of 0.1 mg. of vitamin. At 0.4 mg., the amount of vitamin oxidized by excess nitrite was within the



experimental error. Consequently, the influence of the nitrite ion cannot be significant.

To explain the nitrogen evolution and the yellow color formation observed by him, Barak (2), studying the influence of caustic upon a solution of ascorbic acid and diazotized sulfanilic acid, suggested that the primary alcohol group of the vitamin, functioning as an alcohol, was oxidized to an aldehyde, and the diazonium salt was reduced to a mixture of sodium benzenesulfonate and azobenzene—*p*, *p'*-di-sodium-sulfonate.

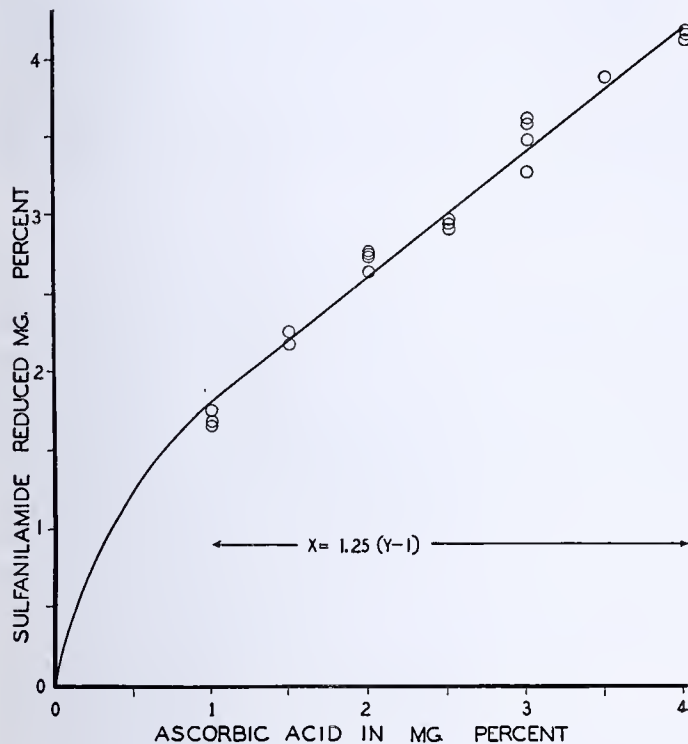
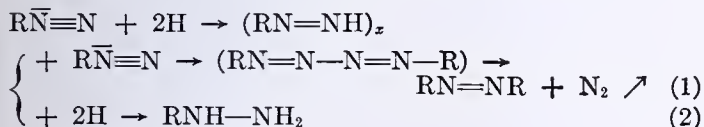


FIGURE 1

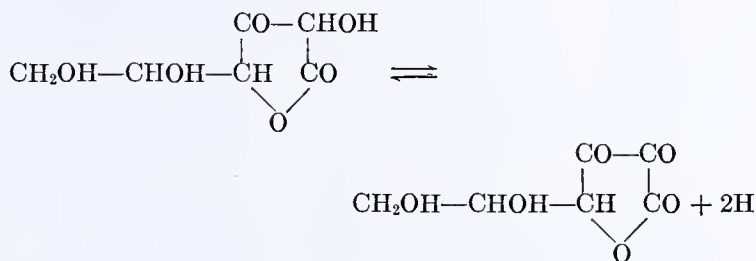
In the present study, the number of molecules of ascorbic acid required to reduce one molecule of diazotized sulfanilamide (Figure 2) increases from 1.1 to 1.9 with increasing vitamin concentrations. The reduction process appears to be instantaneous. Although the 10-minute interval required for maximum azo color development prevents an accurate time measurement, allowing periods of 1 to 30 minutes after the addition of the vitamin gave no measurable difference in the extent of diazonium reduction. Prior to the addition of the beta component, no yellow color was formed in 1 to 30 minutes at low vitamin concentration nor within 1 to 15 minutes at high concentrations. These facts suggest the following reaction mechanism wherein  $(\text{RN}=\text{NH})_2$  the common reduction intermediate is entirely hypothetical, R is equivalent to the *p*-sulfamidobenzene radical, and 2H is equivalent to one molecule of the vitamin:



The absence of alkali diminishes extraneous diazo decomposition, and azobenzene-*p,p'*-disulfonamide (12), if formed, is insoluble in and imparts no discernible color to acidic solutions, although it forms yellow alkaline solutions. The tangent to the curve of Figure 2 at the origin is essentially 60° with respect to the *x*-axis. Reaction 1 requires a slope of approximately 60°. As the concentration of the vitamin increases this angle is reduced to appreciably below 30°. Reaction 2 requires a slope of slightly less than 30°.

At the concentrations studied nitrogen evolution is imperceptible. Nitrogen is evolved at higher concentrations. Measurements of this resultant would yield further insight into the reaction mechanism. In the absence of these data, and in consideration of the complexity of diazonium reduction reactions, the above mechanism must be considered tentative, since the reduction process may result from a series of concomitant reactions. For example, benzenesulfonamide formation, requiring one molecule of vitamin per molecule of diazonium salt, or interaction of ascorbic acid with the hydrazine, involving three moles of the vitamin per mole of diazonium ion, may occur. The curve of Figure 2 does not appear to be influenced by air oxidation, since solutions of the vitamin are stable for longer periods of time than those used.

The simple reversible reaction indicated is not possible, since there is no time factor involved in the reduction process.



Two series of experiments were run in duplicate at vitamin concentrations of 1 and 4 mg. per cent in the 10 cc. of 10 per cent acetic acid. Increasing periods of time, from 1 to 30 minutes, were allowed to elapse before the addition of the 1-dimethylnaphthylamine. At 1 mg. per cent of the vitamin a slight yellow color was formed within 30 minutes. A similar but deeper color was obtained at 4 mg. per cent. (When no 1-dimethylnaphthylamine was added the yellow color intensified considerably on longer standing.) The decrement in the final coupling color in all sixteen experiments was precisely that obtained in the standard procedure. The formation of the yellow color is therefore due to subsequent reactions.

Borsook *et al.* (3) demonstrated that above a pH of 4, dehydroascorbic acid undergoes a nonoxidative, irreversible change, and the initial product was provisionally assigned the structure 2,3-diketo-*l*-gulonic acid. With increasing pH, lactone hydrolysis is followed by a second and third oxidative change. These are not measured in the present method. Borsook observed that 10 mg. per cent of dehydroascorbic acid at a pH of 7 gave rise to a brown-yellow

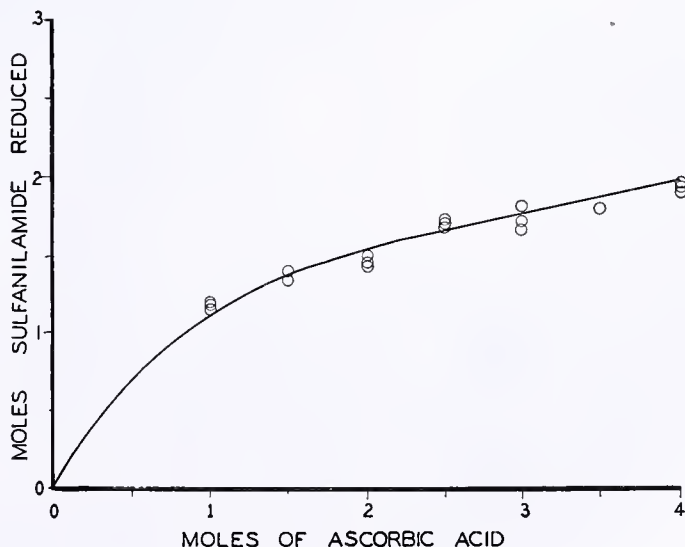


FIGURE 2



color after several hours, and the products responsible for this color did not reduce 2,6-dichlorophenolindophenol. The substances producing the yellow color in the present work can be the same as those observed by Borsook only if lactone hydrolysis of the dehydroascorbic acid can occur at pH values below 4. This does not seem likely from Borsook's work. In accordance with the suggested reaction mechanism, the yellow color may result from hydrazone formation (11).

TABLE III. COMPARISON OF METHODS

Sample and Dilution	Indophenol		Diazo Method	
	Diluted	Un-diluted	Diluted	Un-diluted
Orange juice:				
1:15	0.035	0.53	0.026	0.39
1:20	0.024	0.48	0.020	0.40
1:25	0.018	0.45	0.015	0.36
Orange juice:				
1:15	0.036	0.54	0.025	0.38
1:20	0.021	0.42	0.018	0.36
1:25	0.018	0.45	0.014	0.36
Grapefruit:				
1:15	0.031	0.47	0.026	0.39
1:20	0.026	0.52	0.020	0.40
1:25	0.020	0.50	0.016	0.40
Lemon juice:				
1:15	0.024	0.36	0.022	0.33
1:25	0.014	0.35	0.012	0.30
Grapefruit, canned:				
1:10	0.024	0.24	0.034	0.34
1:25	0.010	0.25	0.013	0.33
Lemon juice:				
1:10	0.033	0.33	0.036	0.36
1:25	...	..	0.014	0.35
Lemon juice:				
1:25	0.012	0.30	0.014	0.35
After 4-5 hours:				
1:25	...	..	0.014	0.35
Orange juice:				
1:15	0.026	0.39	0.029	0.44
After 4-5 hours:				
1:15	...	..	0.025	0.38
1:25	0.016	0.40	0.017	0.42
After 4-5 hours:				
1:25	...	..	0.015	0.38

As indicated by the work of Martius and von Euler (10), cysteine does not interfere in the present method in concentrations up to 10 mg. per cent (given in terms of the concentration of the extraneous reducer in 10 cc. of 10 per cent acetic acid). Borsook has shown that sufficiently high concentrations of glutathione reduce dehydroascorbic acid, that cysteine is one-half as efficient as the tripeptide in this respect, and that this property is characteristic of the thiol group. In this method concentrations of 20 mg. per cent cysteine do not cause variations in the presence of 1 to 4 mg. per cent ascorbic acid.

Barak (1) has shown that imidazoles give a pseudo-phenol diazo reaction in alkaline coupling procedures. Duplicate series using histidine as a representative of this class in concentrations up to 100 mg. per cent did not interfere. High concentrations of ammonia produce yellow casts in the final coupling color. An ammonia concentration of 1 per cent introduces an error of only 8 per cent. Creatinine and uric acid did not interfere in concentrations up to 25 and 6 mg. per cent, respectively.

The gluco-reductones (4) prepared by the method of Kertesz (7) in concentrations equivalent to 5 and 12 mg. per cent, as judged by the 2,6-dichloroindophenol titration, definitely interfere by introducing a yellow cast to the final coupling color as well as a tinctorial decrement. The influence of the reductones is considerably diminished by the acid coupling medium. The marked color decrement produced in neutral coupling media (13) suggests that such procedures may be standardized for the estimation of the gluco-reductones.

Phenol does not interfere in concentrations up to 1 per cent nor tyrosine up to 20 mg. per cent. Hydroquinone produces

pronounced errors at 5 mg. per cent. The specificity phase of this work has not yet been completely elucidated.

In Table III each figure given for the indophenol method represents the average of 4 to 6 titrations. The data for the diazotization method represent duplicate determinations upon the same fruit juices preserved in 10 per cent acetic acid. Two or three determinations were performed upon the same fruit juice at increasing dilution. Multiplying the concentration by the dilution gives a good indication of the consistency of the method.

The present method is too new, and data are too limited to justify an explanation of the differences observed in the above data. Differences in the specificity of both methods seem to exist. In general, the values found by the present method are lower and more consistent than those obtained by a simple indophenol titration. The higher values obtained for the canned sample of grapefruit juice may be due to preservatives.

## Applications

The method has not been applied to blood, since at present too large volumes are required. Difficulty has been encountered in applying the method to urine. Urine preserved with 10 per cent acetic acid imparts yellow casts to the final coupling color. Fairly good results (judged by the indophenol titration) were obtained by adding bromothymol blue to the standard and thus matching the yellow colors prior to the addition of the 1-dimethylnaphthylamine, as in the work of Shinohara (15). However, certain substances in normal urine give a brown-yellow color upon the addition of the nitrite, which is difficult to match. Attempts to remove these interfering substances have not yet been successful.

The use of Lloyd's reagent has been suggested (3) to decolorize the urine. This does not remove the interfering substances when used with metaphosphoric acid. It cannot be used with sulfosalicylic acid, since the dissolved aluminum forms a red chelated coordination complex of the alizarin S type. Addition of caustic does not precipitate hydrated aluminum oxide from this complex, but changes the color to a greenish yellow. Similar results were obtained with refined silica. Sulfosalicylic acid thus appears to be a delicate reagent in such cases.

## Summary

The reduction of diazotized sulfanilamide by ascorbic acid in acidic media has been studied. Stoichiometric relationships suggest that the products are largely phenylhydrazine-*p*-sulfonamide and azobenzene-*p,p'*-disulfonamide. The reduction process is not reversible. The yellow color formed upon long standing is the result of secondary reactions involving the resultants of the initial reduction process.

A quantitative method for the estimation of ascorbic acid has been devised. A calibration curve has been established empirically. From this curve the concentration of ascorbic acid, *X*, in the unknown may be read directly from the concentration of the diazotized sulfanilamide reduced, *Y*. That portion of the curve to which the method is applicable may, within the experimental error, be plotted as a straight line satisfying the expression  $X = 1.25(Y - 1)$ .

Specificity studies have shown that cysteine, tyrosine, histidine, creatinine, ammonia, phenol, and uric acid do not interfere. Hydroquinone and the gluco-reductones interfere. This interference is markedly reduced by coupling in acid media.

Analyses of a series of fruit juices gave satisfactory results as compared with the standard 2,6-dichlorophenolindophenol method. Slight differences, apparently due to specificity differences, exist.



### Acknowledgment

Thanks are due Solomon Weintraub, pathologist, and Jesse G. M. Bullova, visiting physician, for their kind interest in this work. The assistance of Harold W. Grossman and Sidney Recht is greatly appreciated. This study was in part supported by the Metropolitan Life Insurance Company and the Baruch gift.

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## A Powder Measurer

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THE powder measurer is designed to measure, rapidly and fairly accurately, powders of widely varying bulk in small amounts by weight, and fill them into cylindrical vials of small diameter or other containers.

### Construction

The instrument consists of a tube of metal or other suitable material about 12.5 cm. long and 5 mm. in inside diameter, and a plunger bearing at its lower end a cork washer tightly fitting the lumen of the tube. The lower end of the tube (Figure 1) is cut off at right angles and abruptly tapered on the outside with a rounded bevel to a sharp edge on the inside, *a*. The upper part of the tube is provided with a double slot about 3.5 cm. long and 2 mm. wide, extending downward from a point about 2.5 cm. below the top. The outside of the tube is threaded through its upper 6.5 cm. and provided with two check collars, *b*, *c*, and their locking nuts, *d*, *e*. The top of the tube is provided with a hexagonal cap, *a* (Figure 2), perforated with a central hole snugly fitting the shaft of the plunger, and its lock nut, *b*, threaded to fit the outside of the tube. The lower 6 cm. of the tube is thinned to a wall thickness of about 1 mm. The outer surface of this part of the tube is highly polished, as is also its entire inner surface.

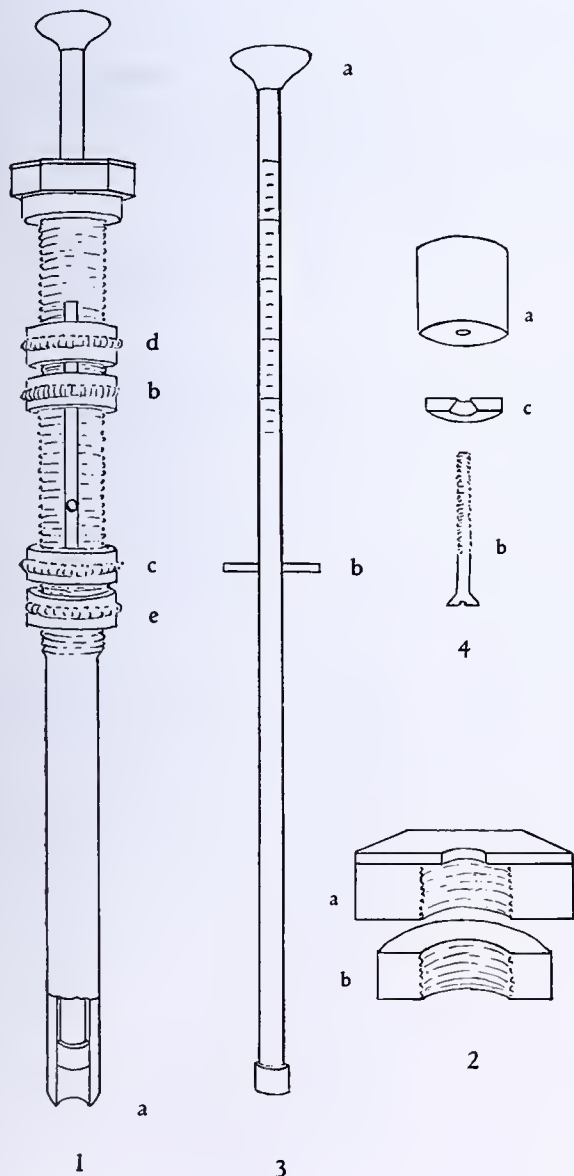
The plunger (Figure 3) consists of a shaft of metal or other suitable material, about 1.5 cm. longer than the tube, and of slightly smaller diameter than its lumen. The upper end is provided with a cap or thumb rest, *a*, about 1 cm. in diameter.

The shaft is drilled and provided with a removable pin (the check pin, *b*), its two ends projecting so as to fit into the slot of the tube when the plunger is in place. When the end of the plunger is flush with the lower end of the tube the check pin is 1 or 2 mm. from the bottom of the slot. The upper part of the shaft is provided with a millimeter scale reading downward from a 0 mark—the point on the shaft opposite the top of the hexagonal cap when the end of the plunger is flush with the end of the tube—and so can be used to measure the variable length of the chamber at the end of the tube for all positions of the plunger.

The lower end of the shaft (Figure 4) is fitted with a perforated cork washer, *a*, which tightly fits inside the tube and is secured to the shaft by a bolt, *b*, and metal washer, *c*. The latter is about 4 mm. in diameter, just narrow enough to clear the walls of the tube yet broad enough to lend sufficient support to the cork. It is drilled and reamed to countersink the head of the bolt and make it flush with the washer.

### Operation

The plunger, with its check pin removed, is inserted in the tube and thrust downward until the lower metal washer is flush with the lower end of the tube. Keeping the plunger in this position, the check pin is passed through the slot and forced into its hole in the shaft of the plunger, and the lower check collar is raised to contact the check pin and locked in position. The plunger is next drawn up to indicate the required reading on the scale, and the upper check collar is screwed down to contact the check pin and locked in position. The instrument is then ready for use with all powders of the same bulkiness or specific powder number. The filler is thrust through the powder held in a narrow cylindrical jar, and firmly pressed against the bottom three or four times or until the chamber of the tube is completely filled.





The powder is then ejected into the required container by forcing down the plunger. In this way the instrument can be made to deliver repeatedly 50 mg., for example, with a variation of not more than 1.3 per cent from the mean and with great rapidity.

A fresh setting of the lower check collar and its accompanying 0 setting of the hexagonal cap are rarely required—only when a worn cork washer is replaced by a new one of different thickness. Fresh settings of the upper check collar are required for each change of specific powder number.

### Determining Specific Powder Number

The specific powder number is a measure of the bulkiness of the powder and is defined as the ratio of the weight of the packed powder to the weight of an equal volume of water at maximum density. It is thus the specific gravity of the combination of air and powder when the powder is packed as tightly as possible. Maximum packing is generally attained by three thrusts through the powder—more only if the powder is unusually fluffy. To determine the specific powder number the upper check collar of the measurer is screwed up out of the way, and the plunger is drawn up to a point on the scale which it is estimated will give the proper chamber length to deliver a convenient amount of powder. The chamber is then filled by an appropriate number of thrusts into the powder mass, and the powder picked up by the filler is ejected onto the pan of a balance and weighed. The specific powder number,  $P$ , may be calculated from

$$P = \frac{W_1}{l_1 \pi r^2} \quad (1)$$

where  $W_1$  is the weight of the powder,  $l_1$  is the length of the chamber as indicated on the scale, and  $r$  is the radius of its cross section, assuming the chamber to be a perfect cylinder.

Different species of pollen afford interesting examples of specific powder numbers. Two species seldom have exactly the same powder number, yet those of closely related species are generally nearly the same:

Name	Powder Number
Tall ragweed, <i>Ambrosia trifida</i>	0.45
Short ragweed, <i>Ambrosia elatior</i>	0.48
Timothy, <i>Phleum pratense</i>	0.725
Bermuda grass, <i>Cynodon dactylon</i>	0.75
Sweet vernalgrass, <i>Anthoxanthum odoratum</i>	0.71
Rocky Mountain yellow pine, <i>Pinus scopulorum</i>	0.375
Colorado fir, <i>Abies concolor</i>	0.375

The specific powder numbers are highly characteristic and may even be used in checking the identities of powders. When the specific number is known, any desired weight of powder may be easily and rapidly measured out by the powder measurer. The length of the chamber or setting of the shaft scale,  $l_2$ , is found from

$$l_2 = \frac{W_2}{P \times \pi r^2} \quad (2)$$

where  $P$  is the specific powder number,  $W_2$  the weight of powder required, and  $r$  the radius of the cross section of the tube.

If the instrument is to be used only to measure out stipulated weights of different powders, it is not necessary to determine their specific powder numbers nor to measure the internal diameter of the tube; it is only necessary to make one trial weighing of each powder, using an arbitrarily chosen chamber length, and from this correct the chamber length for all subsequent measurements of this or any other required weight. The corrected chamber length is the trial length multiplied by the quotient of the required weight over the trial weight. This may be expressed:

$$l_2 = \frac{l_1 \times W_2}{W_1} \quad (3)$$

Mathematically Formula 3 is obtained from 2 by substituting the equivalent for  $P$  in Formula 1.

In actual practice the application of Formula 3 is rapid and easy. If 10 is chosen as the chamber length for the trial weighing, and 50 mg. is the required weight of powder, the corrected chamber length is 500 divided by the trial weight.

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## Determination of Alkoxy by the Method of Vieböck and Schwappach

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IN ATTEMPTING to apply the Vieböck and Schwappach modification (3) of the Zeisel determination of methoxyl, difficulty was encountered in spite of the fact that the method has given excellent results in the hands of others (1, 2).

According to the directions of Vieböck and Schwappach, the addition of formic acid to destroy the excess bromine should give a light-colored solution. In the authors' blank runs this was the case, but when a sample was analyzed, the solution turned darker on the addition of formic acid. Although Vieböck and Schwappach state that if the bromine color is not rapidly destroyed an insufficient amount of acetate is present, use of a larger quantity of acetate did not remedy the difficulty.

After considerable experimentation it was found that insufficient bromine was present originally to oxidize all the iodine monobromide to iodic acid. All previous directions state that 6 to 7 drops of bromine should be added for a 20- to 50-mg. sample, the size of sample to be chosen so that a convenient amount of 0.1  $N$  thiosulfate will be consumed. The authors found that a medicine dropper having an approximately 0.7-mm. opening delivered an average of 0.023

gram of bromine per drop. If 25 cc. of 0.1  $N$  thiosulfate are to be consumed in the final titration, the amount of bromine theoretically necessary would be 0.200 gram or about nine of these drops. In order to ensure an excess of bromine it is desirable to use about 0.3 gram or 0.1 cc. of bromine for each 10 mg. of methoxyl or each 15 mg. of ethoxyl in the sample, each cubic centimeter of 0.1  $N$  thiosulfate being equivalent to about 0.5 mg. of methoxyl or 0.75 mg. of ethoxyl.

Since a lack of sufficient bromine can be detected immediately on adding formic acid, it was thought that such runs might be recovered by adding more bromine at this point. While such a procedure gives approximately correct results, they are by no means as consistent or accurate as when sufficient bromine is present in the original absorbing liquid.

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# Recent Developments in Methods of Testing Germicides

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This is a review and discussion of recent developments in the testing of antiseptics and disinfectants, as well as an attempt to evaluate suggested modifications of present standard methods and proposed new tests. The trend towards more general use of practical testing of germicides is commended, since such tests are valuable not only in showing actual value of germicides under practical conditions of use but also in supporting the use of laboratory tests. The

importance of practical and clinical tests and their possible use in standard methods and in research are emphasized. The recent tendency to test the reaction of germicides on tissues and the value of a toxicity index for antiseptics are discussed. The limitations of some of the proposed new procedures and the promising possibilities of others are considered from the viewpoint of possible use as standard methods for testing germicides.

THERE has been considerable interest in methods of testing antiseptics and disinfectants since publication by the U. S. Department of Agriculture in 1931 of the official methods of test employed by the Food and Drug Administration in the testing and control of these products. The methods of test which were described by the author from 1925 to 1929 (14, 15, 19, 20) were incorporated in U. S. Department of Agriculture Circular 198 (28) and officially designated as the Food and Drug Administration Methods of Testing Antiseptics and Disinfectants in 1931. Since that time much further work has been done in this field. The present paper reviews and attempts to evaluate these recent developments, including not only recent improvements in laboratory methods of testing these preparations, but also laboratory, practical, and clinical tests generally.

## Testing Antiseptics and Disinfectants

Among the present standard laboratory methods of testing antiseptics and disinfectants, probably of most importance at the present time is the recent study on the effect of culture media, especially peptone, on the resistance of *Staphylococcus aureus*, the standard test organism employed in testing antiseptics. The standard resistance of this organism to phenol when tested by the technic employed in the Food and Drug Administration method is that it is not killed by 1 to 60 phenol at 20° C. in 5 minutes nor by 1 to 80 phenol at 37° C. in 5 minutes. When culture media, broth, and nutrient agar are made as described by the author and in Circular 198, the resistance of this test organism seldom varies from this standard of resistance when a suitable peptone is employed.

Peptone made by Armour and Co. is specified in the F. D. A. method and should always be used. For some reason, however, the Armour peptone specially made for this purpose during the past few years has failed to give cultures which uniformly met this standard of resistance. In fact, Meyer and Gathercoal (9) and Vicher, Meyer, and Gathercoal (30) were unable to secure uniform results with this peptone in their studies on the phenol resistance of *Staphylococcus aureus* and as a result recommended to the National Formulary Committee that a somewhat weaker standard be adopted for use in the new National Formulary. This weaker standard was incorporated in the description of the method for testing Liquor Antisepticus adopted as standard by National Formulary VI (10).

It has been shown by the author (23) that the use of such weak cultures gives results in testing germicides which are different than those obtained when cultures of normal standard resistance are used. The whole subject was later restudied by

the Antiseptics Committee of the National Association of Insecticide and Disinfectant Manufacturers (25) and it was proved that media made from regular Armour's peptone gave cultures of normal resistance, whereas the specially purified peptone which had been made especially for this purpose gave weak cultures. Incidentally Burlingame and Reddish (4) restudied the effect of ten different brands of peptone on the resistance of *Staphylococcus aureus* and proved again that Armour's peptone is the most satisfactory for media used in the testing of antiseptics and disinfectants. As a result of this study arrangements were made with the Armour Laboratories whereby each lot of peptone which is set aside for use in testing antiseptics and disinfectants will first be tested and approved by this Antiseptics Committee (24) and then submitted to the Food and Drug Administration before it is made available for use. This tested and approved peptone will always give cultures of normal standard resistance of the test organisms employed in these tests. The importance of this is obvious.

Another recent development had to do with the laboratory method of testing antiseptic lozenges. The author (19) recommends the wet filter paper method, which is also specified as official by the U. S. Department of Agriculture (28) for testing "Solid Soluble Antiseptics: (a) Lozenges, tablets, etc."

However, this class of preparations has often been tested by the method used for liquid antiseptics, first dissolving the lozenge or tablet in water. The justification for this, apparently, is that this method for testing liquid antiseptics is specified for "soluble and liquid antiseptics" and since most lozenges are soluble in water the method has erroneously been used for water-soluble tablets. Because of the liberty taken with this test by many, the author made a special study of the germicidal activity of lozenges containing antiseptics, using both these laboratory methods together with extensive practical tests (21). It was found that those antiseptic lozenges which kill *Staphylococcus aureus* by the standard F. D. A. wet filter paper method will kill very large numbers of bacteria when the lozenge is dissolved in the mouth, reducing their numbers to a significant degree. If, on the other hand, the lozenge does not contain sufficient antiseptic to pass this severe test but does pass the test for liquid antiseptics, it does not kill significant numbers of bacteria when dissolved in the mouth. The results of these practical tests constitute sufficient proof, if any were needed, that the standard F. D. A. wet filter paper method should be used for solid soluble tablets and that the method employed for liquid antiseptics is not a proper test for this purpose.

Recent studies have been made on bacterial reduction in the mouth by means of oral antiseptics and these results compared to those obtained by laboratory tests by the standard method for liquid antiseptics (18). It was found that Liquor Antisepticus N. F. IV, which passes the F. D. A. test for liquid antiseptics, reduces the bacterial count of the mouth and throat 96 to 98 per cent when used as a mouth wash and gargle. This is additional proof that the F. D. A. standard laboratory test for liquid



antiseptics is satisfactory for indicating the germicidal activity and effectiveness of such preparations when used under practical conditions.

### Phenol Coefficient Test

The phenol coefficient test has been employed for determining the germicidal efficiency of disinfectants for thirty-five years, and has served a very useful purpose. One of the uses made of the phenol coefficient of phenol-like disinfectants is for calculating the dilutions to be used in practice. It is generally recognized that a dilution of such disinfectants which is 20 times the phenol coefficient will be equal to 5 per cent carbolic acid when used under practical conditions. This simple means of calculating the proper dilution of phenol-like disinfectants for practical use was recently submitted to test by Varley and Reddish (29) on a large series of such disinfectants of various phenol coefficients. It was found that these compounds when diluted to 20 times their respective phenol coefficients, regardless of what this figure might be, are of sufficient germicidal strength to kill very large and even exaggerated numbers of disease-producing bacteria within a short time under practical conditions of use. In fact, as was expected, such dilutions of these disinfectants were just as germicidal under these practical conditions as 5 per cent carbolic acid. This is additional proof that the phenol coefficient of phenol-like disinfectants is a suitable measure of the practical value of such compounds and that the factor "20 times the phenol coefficient" is a proper means of calculating the dilutions for general use in practice.

These studies in which the results of laboratory and practical tests are correlated are important. The practical tests supplement the laboratory tests, and the results of such comparisons supply additional proof that these standard laboratory tests are adequate for the purpose of indicating the practical value of the preparations so tested. As a result of such studies standard laboratory tests can be employed with confidence.

During the past few years the phenol coefficient test has been widely misused. Although developed for determining the germicidal efficiency of disinfectants which are chemically related to phenol, it has lately been employed for other compounds, for compounds insoluble in water, and for antiseptics of all kinds. This test, as pointed out by the author (16, 22), should be limited to those preparations which are to be used on inanimate objects and to water-soluble compounds, and should never be used for testing antiseptics. These limitations of this valuable test should be recognized by all who are interested in this field.

### Sterilization of Surgical Instruments

It is to be expected that present laboratory methods will be improved from time to time and that new and different tests will be proposed as the need arises. Especially during the past seven years, various chemicals have been recommended for the sterilization of surgical instruments in place of heat sterilization. This so-called "cold sterilization" has the advantage over heat sterilization in that the cutting edge of such instruments is not injured. The F. D. A. method now specified for testing solutions used for treating surgical instruments makes use of *Staphylococcus aureus* as the test organism. Usually this method is adequate, since ordinarily such instruments are not heavily contaminated with pathogenic spore-forming microorganisms. When these preparations are recommended for complete sterilization, as is usual within the past seven years, solutions must kill all microorganisms present, including spores (12). There is, then, a need for a standard laboratory method for testing sterilizing solutions in which spore-forming organisms will be employed.

Preliminary steps have already been taken towards the development of such a method (26). Surgical instruments have first been contaminated with all kinds of skin organisms, including some that form spores, by exposing the instruments to the air, handling in the hands, rubbing on dirty clothing, floors, etc. The contaminated instruments were then plated in nutrient agar and the numbers of spore-forming organisms counted. Instruments similarly contaminated were then treated with a solution of 3 per cent formaldehyde in 85 per cent alcohol and were found to be completely sterilized within 5 minutes at room temperature. When the number of spores ordinarily found on contaminated instruments was increased a hundred fold on similar instruments, this solution of formaldehyde in alcohol was found to sterilize such instruments completely within 10 to 20 minutes at room temperature. The use of one hundred times the number of spores usually found on contaminated instruments is considered a sufficient margin of safety for a laboratory test. This method when perfected should be found satisfactory for testing germicides recommended for the sterilization of surgical instruments.

### Athlete's Foot

The need for another standard laboratory test has also become apparent during the past seven years. Because of the increased prevalence of epidermophytosis (athlete's foot), many fungicides are now recommended for the treatment of this infection, but there is no accepted laboratory test which might be used for testing such preparations. Two or three methods have been employed by different laboratories engaged in testing germicides but none has found general acceptance. A method which appears to be suitable has been used by the author for the past two years and practical and clinical tests indicate that it is satisfactory for this purpose (5).

The following test organisms are employed: *Trichophyton rosaceum*, *Trichophyton rubrum*, *Trichophyton interdigitale*, and *Epidermophyton inguinale*.

Each organism is streaked over the entire surface of Sabouraud's agar in 9-cm. Petri dishes, using a 5-day culture of each organism, and inoculating it by means of a sterile dry cotton swab, each organism being streaked on separate plates. These plates are then incubated at room temperature for 5 days, at the end of which time the agar cultures are cut into 1-cm. squares. The fungicide to be tested is then poured over the surface of the culture so as entirely to flood the plate. At the end of 5, 15, and 30 minutes a square of culture and agar is removed and placed in 10 cc. of sterile broth. The excess fungicide is then washed out of the matted culture by shaking the tube lightly for 5 minutes. At the end of this time the block of culture is removed from the broth and the culture is spread over the surface of a sterile plate of Sabouraud's agar. These plates are then incubated at room temperature for 3 weeks and observed for growth.

An effective fungicide should kill these test organisms within 5 minutes. This may seem an arbitrary figure, but experience has shown that fungicides which kill these organisms within 5 minutes by this test are effective in the treatment of "athlete's foot" as proved by clinical test, and that preparations which do not pass this test in 30 minutes are not effective under practical conditions of use. The standard time period should be between these two points and it is suggested that 5 minutes be used as a margin of safety. Another margin of safety is the large numbers of organisms used in the test and the use of four test organisms instead of one. Present indications are that this test will prove satisfactory.

### Recent Developments

During the past few years many new procedures have been proposed for testing the germicidal activity of antiseptics and



disinfectants. Some are promising, while others have proved disappointing.

Probably the most disappointing is the method suggested by Allen (1), which is supposed to simulate practical conditions to a large degree and to evaluate the actual clinical value of antiseptics more accurately than do our present standard tests (2). For various reasons the method has not been found acceptable and has not been employed by bacteriologists in this country. A careful study by Lewis and Rettger (8) has shown that the test is inaccurate and unreliable, and that little significance may be attached to the results obtained by its use. Since it does not simulate practical conditions and has the disadvantages mentioned, this method offers no promise as an additional test or even a supplementary test for germicides.

One of the most interesting and promising recent suggestions for testing germicides is that of Salle *et al.* (27). It is generally recognized that different antiseptics vary considerably in tissue toxicity; in fact, toxicity tests have been suggested as supplementary tests for antiseptics from time to time. Salle and his associates, however, have made the definite suggestion that such preparations can best be evaluated by means of a toxicity index. This figure would represent the ratio between the highest dilution of germicide required to prevent the growth of embryonic chick heart tissue and the dilution required to kill the bacterial test organisms. Much valuable information can be obtained regarding the suitability of antiseptics for different purposes by determining the toxicity index and this method should and no doubt will be widely used.

Considerable interest has recently been shown in methods of testing antiseptic ointments. Making use of the standard F. D. A. agar plate method, Bryan (3) suggests the use of a mercury ointment coefficient as a means of comparing the bacteriostatic activity of antiseptic ointments. Since there is no standard of comparison in our present standard method (17), such as the phenol coefficient test for disinfectants, the adoption of a mercury ointment coefficient is highly desirable. The use of ammoniated mercury ointment, U. S. P., is suggested by Bryan and seems suitable as a standard for comparison, and should be generally employed for this purpose. Such a standard of comparison would tend to raise the quality of such preparations and this is not only desirable but necessary.

Husa and Radin (7) have stimulated considerable interest in this subject by their study of the variations in ointment bases on the antiseptic value of phenol ointments. Vicher, Snyder, and Gathercoal (31) have also shown that other factors, such as size of particles of the active ingredient, calomel, affect greatly the antiseptic value of calomel ointment. Prout and Strickland (13) have studied the effect of fatty and non-fatty ointment bases on antiseptic activity. Other studies in this field are planned which will contribute information on the correlation of results of laboratory and clinical tests on antiseptic ointments and will be especially helpful in interpreting results of laboratory tests in terms of practical values.

Recently some effort has been made to get away entirely from laboratory methods of testing germicides and to use clinical and practical testing instead. Hunt (6) has become an exponent of this method of determining the actual value of antiseptics when used under conditions of practical use. He suggests the application of antiseptics to cutaneous lesions in mice as a means of testing germicidal value of such preparations. By this means the therapeutic value of antiseptics may be evaluated by testing them directly on artificially infected tissue. While such information is valuable, it is extremely difficult if not impossible to standardize such technic so that concordant results may be obtained by different investigators. For this and other reasons Hunt's method

offers little promise as a standard method of testing germicides, but should be found valuable for research in therapeutic studies in this field.

Salle (27) and Nye (11), on the other hand, retain the well-standardized laboratory methods and in addition make use of tests on tissue toxicity. This is a step in the right direction and offers far more promise than strictly clinical tests, at least for general use. Future work on methods of testing germicides should retain as much as possible of the desirable features of present standard laboratory methods but make use of such supplementary practical and clinical tests as may give additional desirable information. A combination of laboratory and practical tests will very probably give sufficient information for the proper evaluation of the efficiency of antiseptics and disinfectants.

## Summary

During the past seven years many new procedures have been proposed. There is a trend towards the use of practical testing of germicides, useful in substantiating results obtained by means of laboratory tests and also possibly supplementing present standard methods. The tendency to test germicides for tissue reactions is emphasized and the use of a toxicity index for antiseptics is discussed. The importance of practical and clinical tests and their possible use in standard methods and for research is considered in the light of present knowledge of the subject.

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# Oxygen Pressure Aging

## Improved Equipment

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An oxygen pressure-aging apparatus is described, which presents the following improvements: (1) small stainless-steel, quick closing jacketed pressure vessels which are easily removable from the system for repair purposes and can be operated singly or in series; (2) an electrically heated, constant-temperature system which can be adjusted to maintain a constant temperature in the pressure-aging vessel at  $70^{\circ}\text{C}.$ , and is readily adjustable to a wide temperature range, depending on the liquid used for the heat transfer; (3) a valve which automatically closes the oxygen supply to the pressure vessel if the safety releases, conserving oxygen and preventing loss of tests in other pressure vessels attached to the same oxygen supply; and (4) a simple, easily operated safety release.

SINCE the introduction of the oxygen pressure-aging test by Bierer and Davis (1), prevailing standard conditions for the test have been  $70^{\circ}\text{C}.$  ( $158^{\circ}\text{F}.$ ) and 300 pounds per square inch oxygen pressure. Various types of equipment have been used; usually the equipment has consisted of a pressure vessel immersed in a constant-temperature water bath to which is connected an oxygen supply. In the ma-

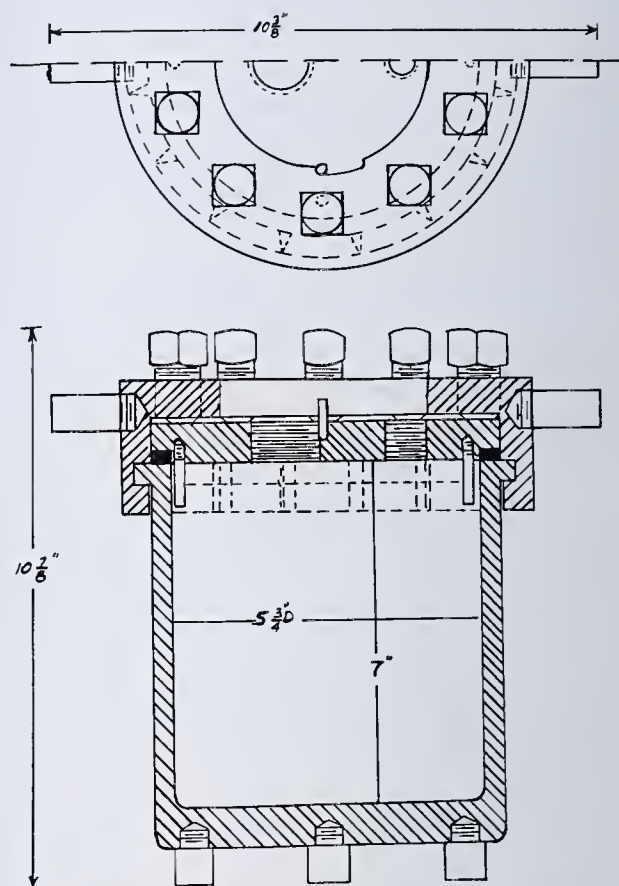


FIGURE 2. PRESSURE VESSEL BEFORE JACKETING

jority of instances the equipment has been difficult to operate and maintain for several reasons:

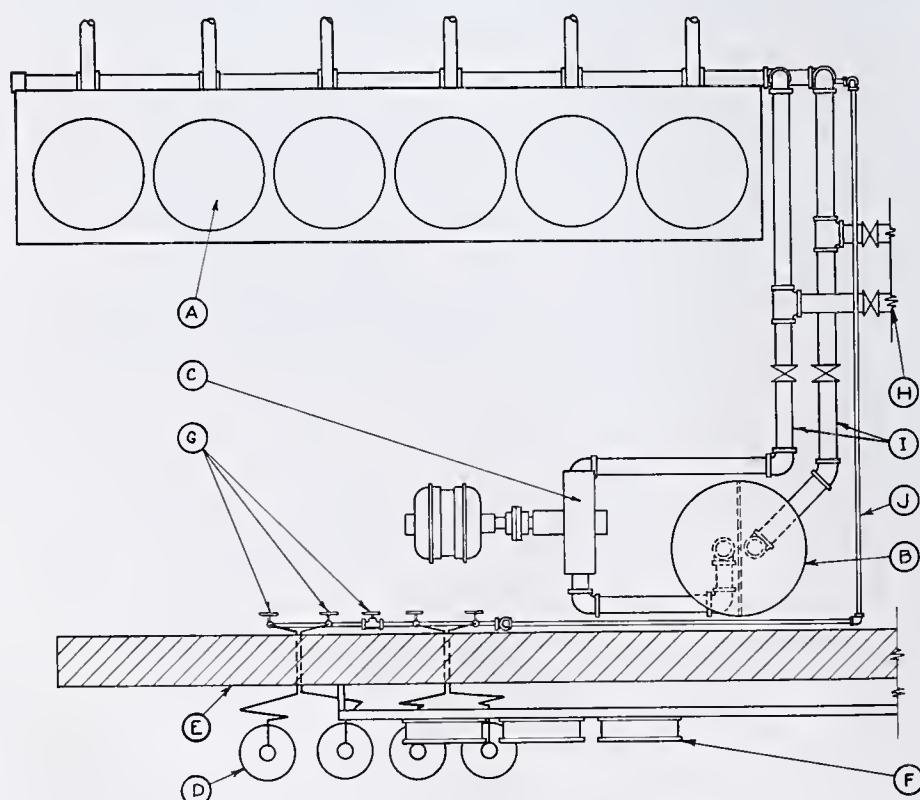


FIGURE 1. INSTALLATION DIAGRAM

Immersion of pressure vessels in a water bath which made handling difficult. Corrosion was a continuous source of trouble, causing "freezing" of cover bolts and making it difficult to obtain a leakproof oxygen seal between cover and vessel. This caused loss of oxygen.

Each time the pressure vessel was removed from the bath it was necessary to disconnect the oxygen supply and make the connection again when the test was started. This also caused loss of oxygen.

If more than one pressure vessel was connected to the oxygen supply and a safety released, the entire oxygen supply was exhausted.

The original pressure vessels were relatively large. Since the use of age resistors on a large scale, smaller units have been desirable in order to decrease migration of age resistors and eliminate erroneous results.

Some of these operation difficulties were outlined by Ingmanson and Kemp (2), who also emphasized the importance of temperature control to obtain reproducible results.

It is the purpose of this paper to describe an improved oxygen pressure installation which avoids some of these difficulties.



## Installation

Figure 1 is a chart showing one of two duplicate installations.

A crossover, *H*, connects the two circulating systems, so that if one of the constant-temperature supply tanks or circulating pumps must be repaired the entire oxygen system can be operated from the other supply. The pressure vessels, *A*, are jacketed and mounted on a steel table. The heat-transfer medium at present is water, which is maintained at constant temperature in tank *B* and circulated around the pressure vessels by circulating pump *C* through pipes *I*. The oxygen supply tanks, *D*, are on the opposite side of a brick wall, *E*, from the aging equipment. The instrument panel, *F*, is adjacent to the oxygen supply, so that the operator can read the instruments and shut off the oxygen pressure or temperature controls while on the opposite side of the brick wall from the pressure vessels. The oxygen supply is con-

nected through reducing valves *G* and pipe *J* to the pressure vessels.

The pressure vessels are of two types:

1. Steel, inside diameter 5 inches and 11 inches high, jacketed so that a heat-transfer medium may be circulated around the vessel. The covers are fastened on with ten bolts.
2. Stainless-steel,  $5.75 \times 7$  inches high (Figure 2 is a drawing of the pressure vessel before jacketing), jacketed so that a heat-transfer medium may be circulated around the vessel. The cover consists of a circular disk which rests on a scaling ring and is held in place by a slide ring. An eighth turn of the slide ring locks it in place over the flange of the pressure vessel and then by means of ten set screws mounted through the ring, all impinging on the cover, a leakproof seal is easily obtained.

Figure 3 is a photograph of the heating system, showing how the electric immersion heaters are installed. The cir-

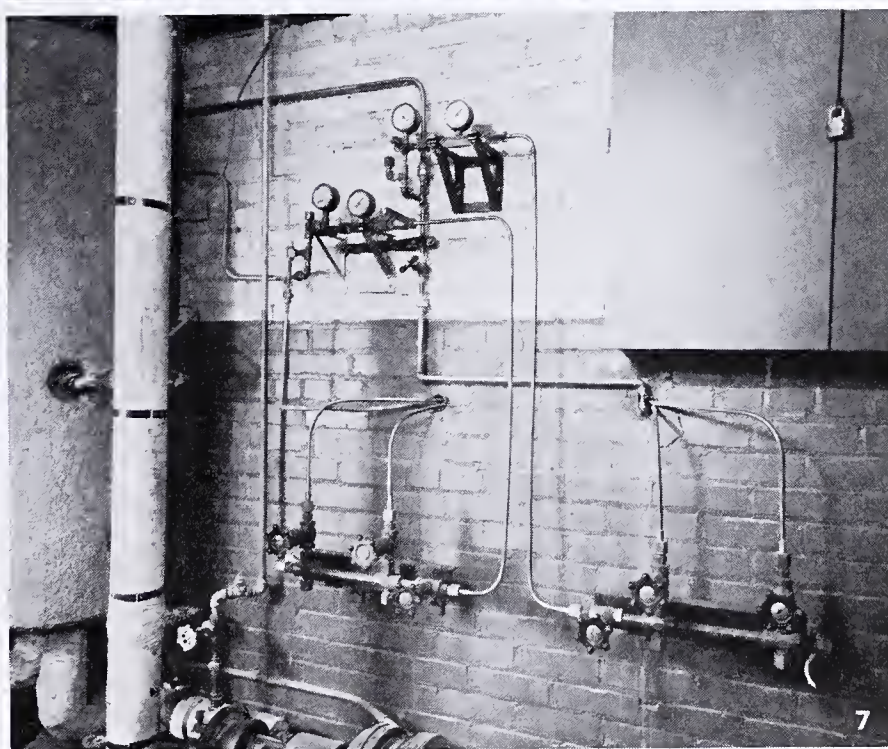
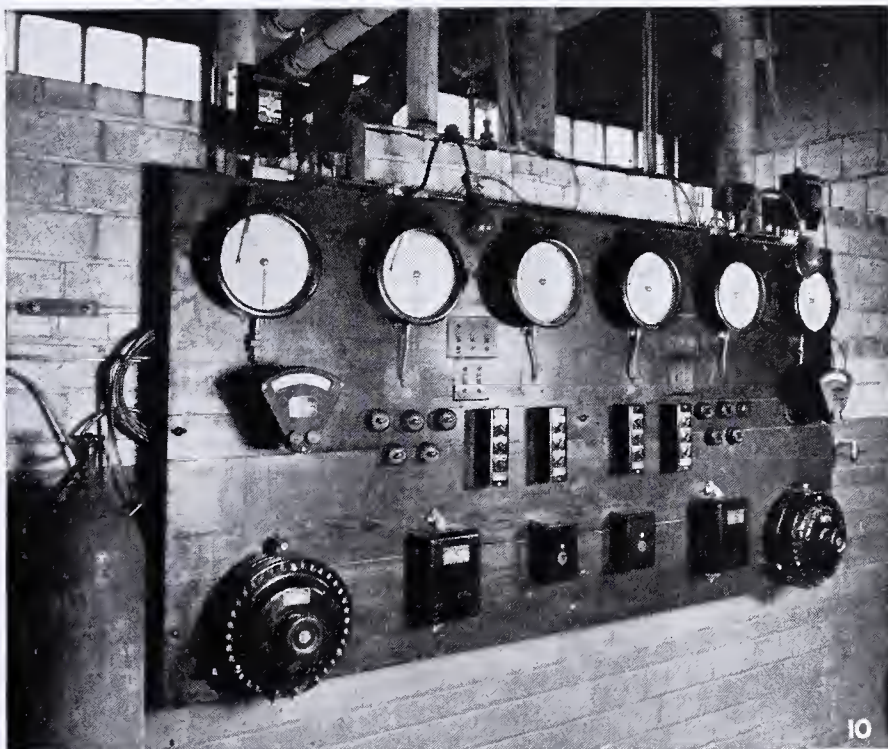
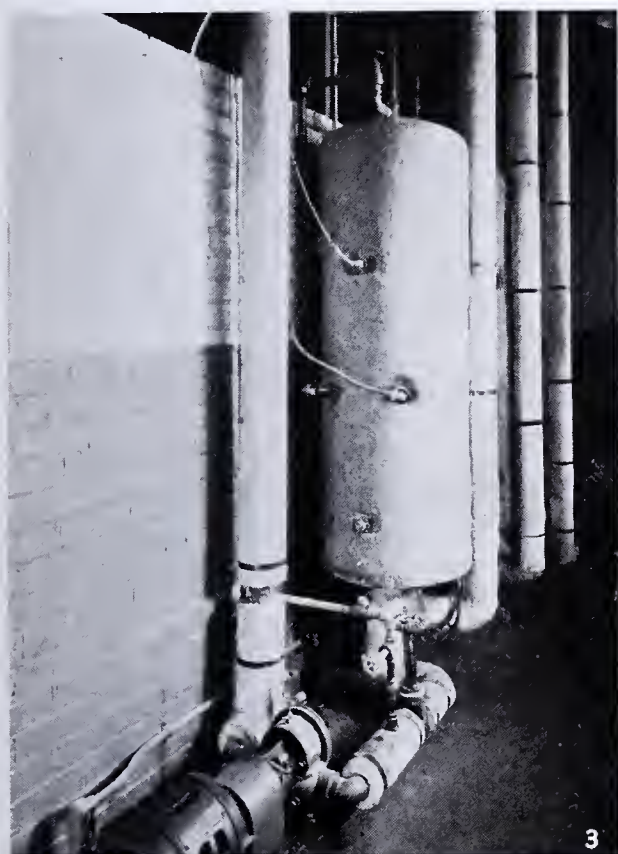


FIGURE 3. HEATING SYSTEM  
FIGURE 6. PRESSURE VESSEL IN PLACE

FIGURE 7. REDUCING VALVES  
FIGURE 10. INSTRUMENT PANEL



culating pump and motor are shown in the lower left-hand corner. Figure 4 is a drawing of the heating tank.

The water returns from the jacketed pressure vessel through pipe *A*, is forced up past heaters *B* and over baffle plate *C* down past temperature controller *D* and heaters *E*, through pipe *F* and circulating pump to the pressure vessels. Recording thermometers in pipes *F* and *A* indicate the temperature of the water before entering the pressure vessel jacket and upon return to the constant-temperature supply tank. To date the differential between these two recordings has been less than 0.5° C. (0.9° F.). The temperature bulb, *G*, actuates an automatic cutoff which is installed in the immersion heater circuit. This cutoff is adjusted to 77° C. (170.6° F.) when the operating temperature is 70° C. (158° F.) and is necessary in order to protect the apparatus in case the circulating system stops.

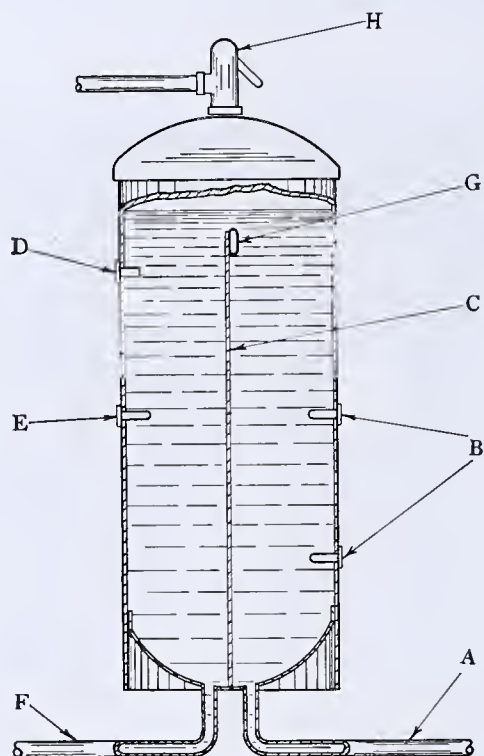


FIGURE 4. HEATING TANK

Figure 5 is a drawing and Figure 6 a photograph of a pressure vessel mounted in place. In Figure 5 the oxygen connection with safety mounting is shown at *A* and the water connections at *I*. The thermometer serves to show whether or not the water is circulating around the individual pressure vessel. It is possible to remove any individual pressure vessel very easily without interfering with the remainder of the system by closing the valves to the circulating system line and to the oxygen supply line, and disconnecting the unions.

The oxygen pressure is supplied from the tanks in Figure 1 through the reducing valves shown in Figure 7.

Between each pressure vessel and the oxygen supply line there is an automatic cutoff valve shown at *B* in Figure 5 and in detail in Figure 8. The oxygen supply from the reducing valve enters the automatic cutoff valve through line *A*. The valve is actuated by a diaphragm, *D*, and by opening valve *C* the oxygen is released to the pressure vessel through line *G* and the pressure on both sides of the diaphragm is equalized through *F* and *B*. When the pressure is equal on both sides of the diaphragm, spring *H* opens valve *E*; valve *C* is then closed and if there is only a small leak through the pressure vessel system oxygen can feed through valve *E*; however, if pressure builds up in the pressure vessel and the safety releases,

then the pressure is released through *F* on one side of the valve and the diaphragm immediately closes valve *E*. These valves operate so rapidly that it is impossible to determine on the pressure-recording chart the time at which a safety has released.

Figure 9 illustrates the safety release—a disk of stainless-steel sheet mounted between tin disks in a compression seal. When the system is operating at 300 pounds per square inch the thickness of the disk is adjusted so that it releases at 350 pounds per square inch.

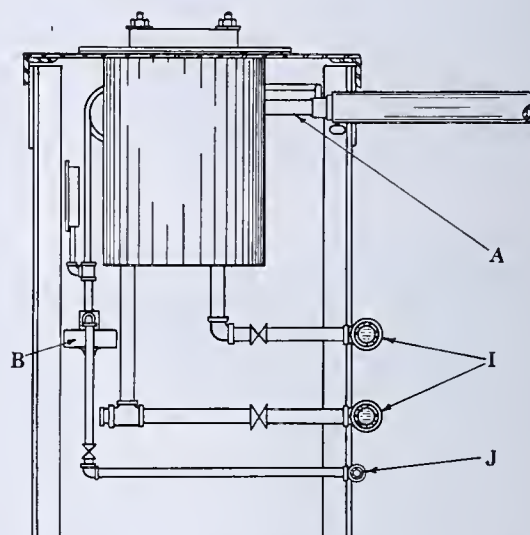


FIGURE 5. PRESSURE VESSEL IN PLACE

The instrument panel shown in Figure 10 has two complete sets of instruments to record and control the operations of the two aging units.

Across the top of the panel are six recording instruments. The two pressure recorders are at the extreme ends; between these are the two pairs of temperature recorders connected to the return and outgo lines from the constant-temperature tanks. Below the pressure recorders are the temperature controllers for the constant-temperature tanks. These controllers actuate the heaters illustrated at *B* in Figure 4. The upper row of the two sets of snap switches controls the heaters which are connected through the temperature controllers; the lower pair of the two sets controls the booster heaters, *E* (Figure 4). The other two pairs of switches can be adjusted so that heaters *B* (Figure 4) are connected separately or in any combination through the rheostats at the lower corners of the instrument panel to the thermometer controller or so that the heaters are connected direct to the thermometer controller. This makes possible a very accurate adjustment of the constant-temperature control. Just below each set of temperature recorders are lights in parallel with the heaters

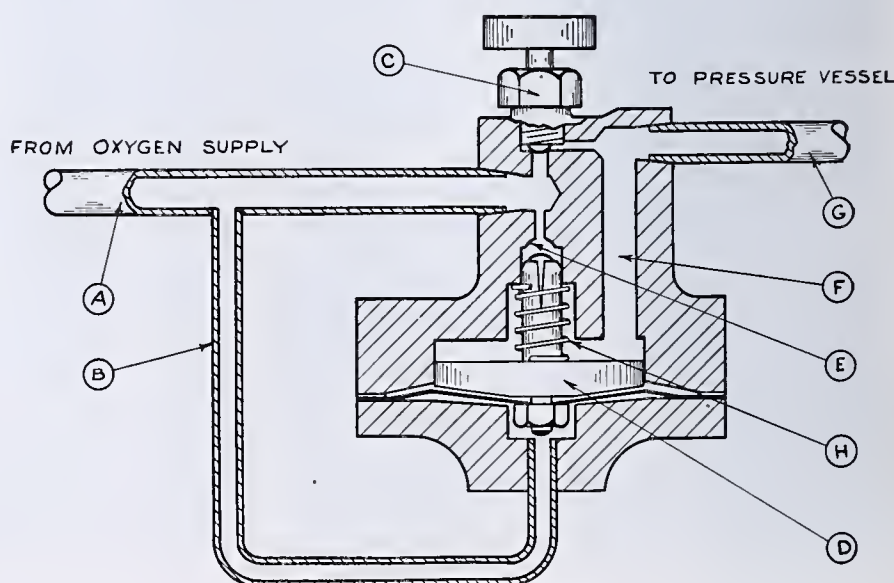


FIGURE 8. AUTOMATIC CUTOFF VALVE



to show which heaters are in operation. Above the instrument panel and adjacent to the main supply line switches are the automatic cutoff switches which connect with bulb *G* in the constant-temperature tank.

### Temperature inside Pressure Vessels

The original plans for the equipment specified that the pressure vessels be bolted to the metal tables, using a gasket to insulate the pressure vessel from the table. After the installation was made according to these plans the following temperatures were obtained inside the 5 × 11 inch pressure vessel:

Position inside Pressure Vessel Inches from top	Temperature ° C.	Water Temperature ° C.
1	68.5	70
3	68.5	70
4	69.0	70
6	69.5	70
7	70.0	70
10	70.0	70

Similar readings inside the 5.75 × 7 inch stainless-steel vessels were low and more variable. In order to correct this variation within the pressure vessel, the tables were covered with Celotex and the pressure vessels then mounted in place.

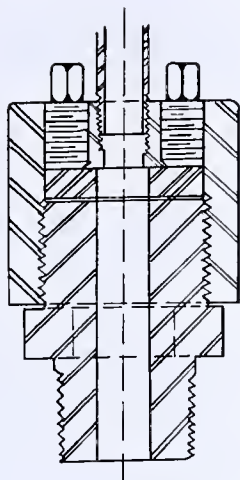


FIGURE 9. SAFETY RELEASE

A wooden top was then fitted over the Celotex and around the lids of the pressure vessel covers. Covers of wood and Celotex were made to place over the pressure vessels and temperature readings inside the 5.75 × 7 inch stainless-steel vessels were as follows:

Position inside Pressure Vessel	Temperature ° C.	Water Temperature ° C.
1 inch from top	69.5	70
1 inch from bottom	69.5	70

With these data available it is possible to adjust the temperature of the circulating water to maintain 70° C. (158° F.) inside the pressure vessels.

Aging studies making use of the flexible facilities of this improved oxygen pressure-aging apparatus will be presented later.

### Acknowledgment

Acknowledgment is made to N. E. Raber of the B. F. Goodrich Engineering Department, who designed the automatic cutoff valve (Figure 8).

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RECEIVED April 2, 1938. Presented before the Division of Rubber Chemistry, American Chemical Society, at its meeting in Detroit, Mich., March 28 and 29, 1938.

## Determination of Formaldehyde in Dilute Solutions and in the Presence of Interfering Substances

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A FLUID pharmaceutical preparation, which at the time of analysis contained about 0.003 per cent of formaldehyde, could not be even roughly analyzed for its formaldehyde content by the ammonia (2), cyanide (1, 5), hydrogen peroxide (3), and iodine (6) methods. This was due in part to the flavoring agent, one ingredient of which was oil of cinnamon (aldehyde). The deep red color of the preparation prevented the use of procedures depending upon production of colors. On attempting to isolate the formaldehyde by distillation, it was found that the small amount of formaldehyde present was reduced to practically zero.

Satisfactory results were obtained with a modification of the silver method (4) used with mixtures of known formaldehyde content. This modification has also the advantage that reducing sugars do not interfere.

### Procedure

Exhaust the aqueous or aqueous alcoholic fluid with ether-petroleum ether (1 + 2) to remove flavor, etc. Four to five extractions, each with one-half volume of solvent, are usually sufficient. To 10-cc. aliquot, add in rapid succession 100 cc. of 0.1 *M* silver nitrate, 1 cc. of hydrochloric acid (37 per cent), and 3 cc. of sodium hydroxide (25 per cent). Whirl once after each addition. Finally whirl 10 minutes for good contact. Filter through paper and wash until chloride free. Pour warm nitric acid (1 + 3) onto precipitate to dissolve all reduced silver. Wash with hot water and titrate with 0.1 *N* ammonium thiocyanate and ferric alum. 2 Ag = 1CH<sub>2</sub>O.

A determination can be done in about 30 minutes. The average percentage reproducibility observed is of the order of two units in the third decimal place.

A mixture was made of 10 cc. of the sample under investigation plus 10 cc. of an aqueous 0.20 per cent formaldehyde, newly made up from about 37 per cent stock and for the purpose of introducing all like interfering factors, also shaken out with the ether-petroleum ether. This mixture analyzed 0.097 per cent; the actual content was calculated as 0.101 per cent (the average of 0.003 and 0.20 per cent).

The aqueous 0.20 per cent formaldehyde made from about 37 per cent stock analyzed 0.19 per cent formaldehyde. After extracting with ether-petroleum ether, it still showed 0.19 per cent, while the Association of Official Agricultural Chemists cyanide method gave 0.009 per cent in both cases.

An approximately 0.2 per cent solution of acetaldehyde, a little freshly made silver chloride, and a slight excess of sodium hydroxide turn the silver chloride a light bluish gray after about one minute, whereas 0.2 per cent formaldehyde, under the same conditions, turns the silver chloride black immediately.

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# An Apparatus for Electrometric Titrations of High Precision

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THE apparatus described below was designed to meet the demand for a convenient titration apparatus suitable for all kinds of titrations. The special stirring device was found to eliminate the difficulties encountered with ordinary stirrers in foaming solutions. This apparatus during two years' use has proved to be very suitable.

The titration vessel (Figure 1) is pear-shaped and has a total volume of about 125 cc. The pear form makes it possible to use from 20 to 100 cc. of solution for a titration. On the upper surface, the vessel has five interchangeable ground joints. For measurements with glass electrodes, the MacInnes type of electrode used is held in the central joint by means of a paraffined cork stopper; for hydrogen-electrode measurements, the central joint is used for the gas inlet and outlet. Calomel and other electrodes, burets, etc., are carried by the peripheral joints. These joints and their accessories have glass hooks and are held together by rubber bands.

The stirring device is shown in Figure 2. The titration vessel with attached accessories is fixed to the stirring device by an easily detachable metal clamp, *A*, around the central joint. This clamp, on the other hand, is mounted on two vertical rods, *B*, in such a way that it can be moved vertically and fixed by screws, *C*, in a suitable position. The vertical rods, *B*, are fixed to the upper part of a cross slide, *D*, the lower part of which is screwed to the aluminum U-rod, *E*, which is fixed across the thermostat vessel. By means of an adjustable eccentric, *F*, and the cross slide, *D*, an electric motor gives the titration vessel a rotatory movement in the horizontal plane. The radius of the eccentric

and the motor speed are adjusted to give the desired radius and speed of rotation. Stirring is obtained by the rotation, which makes the electrodes rotate relative to the liquid. A separate stirrer is superfluous and although a very effective stirring is thus obtained, the titration vessel moves perfectly steadily; consequently long burets need only be held by their interchangeable ground joint at the lower end and there is no fear of breaking the thin membranes of the glass electrodes.

The design of the lower end of the burets is shown in Figure 3. Below the stopcock, the bore is capillary, about 0.5 mm. in internal diameter. If the tip only is capillary, light precipitates in the solution may enter the tip and lie beneath the stopcock. When the bore is capillary all the way up to the stopcock, any

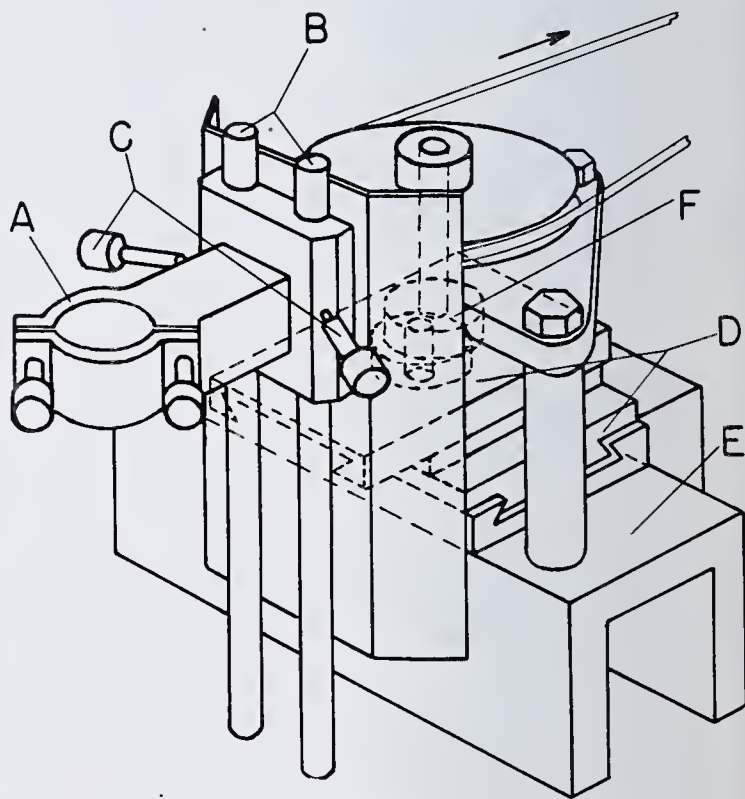


FIGURE 2

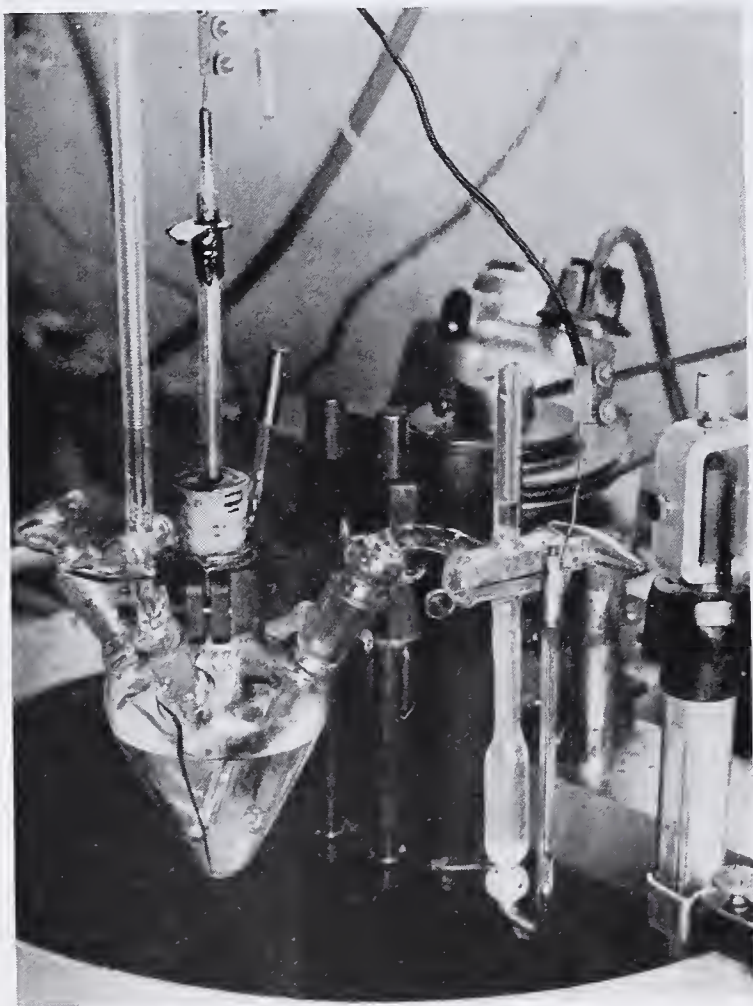


FIGURE 1

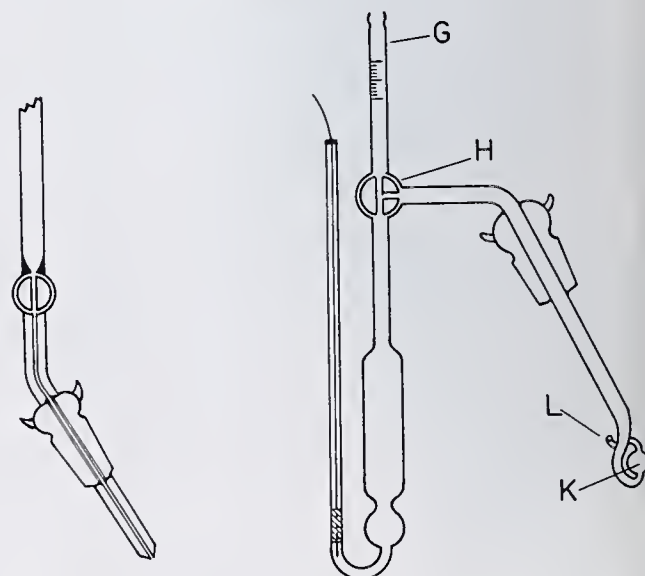


FIGURE 3

FIGURE 4



precipitates which have entered the buret tip can easily be washed out.

The type of calomel electrode used is shown in Figure 4. The goose-neck type of liquid junction, described by Clark (1), has proved to be the most suitable for an apparatus of this kind. The liquid junction is made by applying gentle suction at *G* with stopcock *H* slightly open and *L* dipping into the solution to be examined. The solution flows into the small bulb, *K*, and a sharp junction with the heavy potassium chloride solution can be formed in the middle of bulb *K*. This procedure is facilitated by a calibration on tube *G*. The capillary, *L*, has a length of about 8 mm. and an internal diameter of 1 mm. There is no detectable diffusion of potassium chloride into the solution in the vessel during the time required for an experiment, when using this form of liquid junction. Agar-agar bridges, on the other hand, allow fairly large amounts of salt to diffuse into the solution to be titrated.

An aluminum vessel serves as an oil thermostat. The oil used is a mixture of equal parts of transformer oil (Shell K 2) and white spirit. This mixture does not smell or evaporate and has about the optimal viscosity. All metal parts are earthed. No further

screening is necessary, and glass electrodes give perfectly steady potentials even when stirring.

The freedom from rubber connections makes the apparatus very suitable for titrations in organic solvents. Furthermore, the absence of any external stirrer simplifies titrations which have to be carried out in an inert gas atmosphere.

The photograph in Figure 1 shows the apparatus ready to be lowered into the oil bath for an experiment. All glass parts are made from Pyrex or Jena glass. A microapparatus has been constructed on the same lines, taking from 2 to 10 cc. of solution to be examined.

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RECEIVED April 26, 1938.

## Determination of Sulfur in Some of the More Common Alloys

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THE copper chloride-perchloric acid method (2) for sulfur is applicable to certain ferroalloys as well as to many nonferrous alloys.

### Brass

Bureau of Standards Sample No. 63 may be considered representative. Its percentage composition is: S 0.06, Cu 78.05, Pb 9.74, Sn 9.91, Sb 0.55, As 0.19, Zn 0.48, Fe 0.27, and P 0.62. The Bureau of Standards method is based on the preliminary separation of tin oxide, the removal of copper and lead by electrodeposition, and the removal of nitric acid by hydrochloric acid and heat. The proposed method is more rapid, requires much less manipulation, and is less difficult. The results indicate the same order of precision, but are 0.01 per cent higher in value.

**PROCEDURE.** Transfer 5 grams of brass to a 600-cc. beaker and cover with 500 cc. of potassium-copper chloride solution. Maintain the solution at about 90° C. as on a steam bath. Mechanical stirring is preferred. Keep the solution covered as much as possible.

When all copper has dissolved, filter the warm solution through a fast filter paper, and wash with hot water. Remove the paper from the funnel, place it in the beaker, cover with strong bromine water, and agitate with a glass rod. Add 10 cc. of zinc oxide-nitric acid solution and 8 cc. of perchloric acid. Heat the beaker to destroy the paper and to drive out the nitric acid and the excess perchloric acid. When perchloric acid begins to condense at the top of the beaker, remove the beaker from the hot plate and allow to cool.

Dissolve the residue, usually solid, in water, dilute to about 100 cc., and boil to remove chlorine. Filter off any insoluble matter on paper, and wash with hot water. Dilute the filtrate to 200 cc. and precipitate sulfates with barium chloride. The weight of barium sulfate divided by 5 and multiplied by 0.1373 gives the weight of sulfur found per gram.

**REAGENTS:** 500 grams of  $(\text{KCl})_2\text{-CuCl}_2\cdot 2\text{H}_2\text{O}$ , 100 cc. of hydrochloric acid, and 2000 cc. of water. Sift 200 grams of zinc oxide into 1 liter of concentrated nitric acid.

**RESULTS:** 0.072, 0.071, and 0.070.

### Nonferrous Alloys

The same procedure has been applied to pure copper and to its alloys of tin, lead, zinc, iron, and aluminum; to various

types of monels; and to nickels, cobalts, and nickel-cobalt alloys. These latter dissolve rather slowly.

### Ferromanganese

Using Bureau of Standards No. 68 (S, 0.014 per cent) as a test sample, it was found that the copper chloride solution must be added cold, after which the procedure is as usual for ordinary steels. Results: 0.014, 0.013 per cent. Manganese metals seemed to contain not more than 0.003 per cent of sulfur.

### Ferromolybdenum

Lundell (1) used a hot tube method, or an aqua regia solution method. Apparatus for the first is not usually available, and for the second method the advantages of the copper chloride method apply (2). The only modifications to be applied to the above procedure are:

A smaller sample is used: 3 grams.

Agitation of the alloy in copper chloride solution must be continued until nearly all the iron and molybdenum are dissolved.

In the third paragraph of the procedure, the insoluble matter contains molybdic acid and is washed with hot 0.5 per cent (by volume) hydrochloric acid instead of distilled water.

With these extra precautions not more than 0.0002 gram of molybdenum was found in any barium sulfate precipitates of ferromolybdenum. Converting this value to barium molybdate and calculating to sulfur, no error was found in reporting the result as pure sulfur (to two significant figures). Results: No. 30747: 0.11, 0.11, 0.11, 0.12. No. 4626: 0.25 (1), 0.22, 0.23.

The results obtained with brass and ferromolybdenum were checked by Owen Gates, U. S. Navy Laboratory, Munhall, Pa.

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RECEIVED April 21, 1938.



# An Electronic Voltage Regulator

### With Supplementary Circuit to Supply Low Voltages

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ELECTRONIC voltage regulators have been known to communication engineers for several years, but apparently none has been described in any publication available to chemists. A simple circuit with limited voltage range for use with a moisture tester is described by Working (1), but the circuit shown in Figure 1 gives a much wider voltage range, and at the same time improves the voltage regulation.

## Theory of Operation

To secure voltage regulation, an approximately fixed voltage above the negative side of the line is established by means of a gas-discharge tube (a neon glow lamp with resistor removed from the base, or a type 874), in series with current-limiting resistors. This voltage is applied to the cathode of a tube of high amplification, such as type 6J7. A bleeder across the output which is to be regulated is tapped at a point which will be approximately 3 volts negative to the fixed voltage when the output is at the voltage desired, and this tap is connected to the grid of the 6J7. Any change in output voltage is thus amplified and is applied to the grid of a power tube, as a type 6L6, placed in the positive line to carry the entire output current.

Assuming this simple circuit, an increase in input voltage tends to increase the output voltage, and thus the grid voltage of the 6J7. The increased plate current of this tube lowers the voltage on the grid of the 6L6, thus preventing more than a very slight rise in output voltage. If very precise measurements are made, the gas-discharge tube will be found to have increased slightly in voltage, and altogether for a 10-volt

increase in input voltage the output voltage will increase perhaps 0.1 volt under favorable conditions; much more than that if the tubes are operating outside their range of high sensitivity.

The foregoing assumes a constant screen voltage for the 6J7, but if this voltage be taken from a tap on the resistor which supplies the gas-discharge tube, it will increase with a rise in input voltage and further reduce the plate current of the 6L6. By using a resistor with an adjustable tap the screen voltage may be adjusted to balance exactly, over a limited range, the tendency of the output voltage to change in the same direction as the input. However, if the screen voltage is set at about 100 volts for maximum sensitivity of the 6J7, it will ordinarily overcompensate for voltage changes in the input. Accordingly a second gas-discharge tube is used,  $N_2$  (Figure 1), considerably reducing the fluctuations in screen voltage.

### Circuit Details

The components specified under Figure 1 were chosen to be capable of supplying 60 milliamperes at 343 volts as required by the titrimeter described by Working (2), with line voltage fluctuations up to  $\pm 13$  per cent. However, if the transformer output is only 500 volts, the regulator is operating near its upper limit at this rating, and accordingly the bleeder,  $R_4, R_5, R_6$ , is chosen to have a fairly high resistance in order to put no unnecessary current drain on the output. If this circuit is to be used to supply an instrument using a very small current during part or all of its operation, this will require

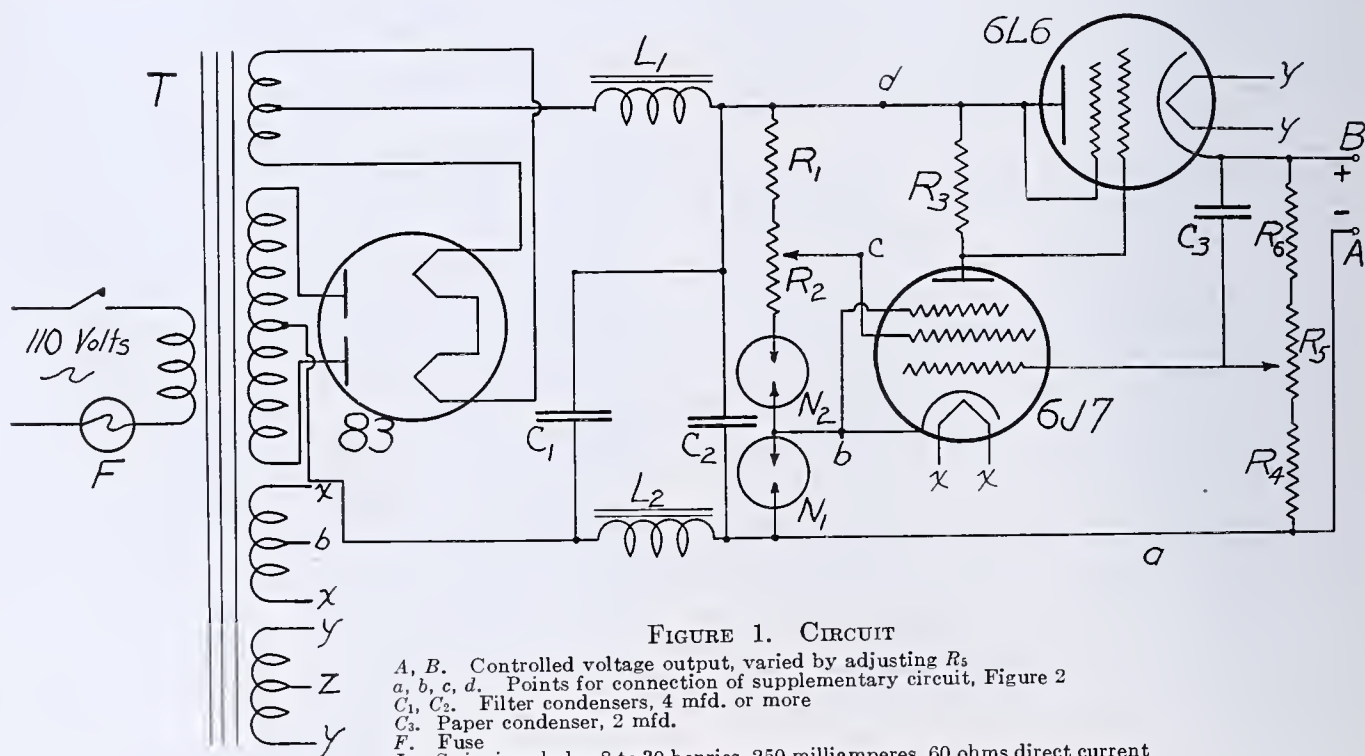


FIGURE 1. CIRCUIT

- A, B. Controlled voltage output, varied by adjusting  $R_5$
- a, b, c, d. Points for connection of supplementary circuit, Figure 2
- $C_1, C_2$ . Filter capacitors, 4 mfd. or more
- $C_3$ . Paper condenser, 2 mfd.
- F. Fuse
- $L_1$ . Swinging choke, 8 to 30 henries, 250 milliamperes, 60 ohms direct current
- $L_2$ . Filter choke, 20 henries, 200 milliamperes, 100 ohms direct current
- $N_1, N_2$ . Neon glow lamps, 2 or 3 watts, with resistor removed from base
- $R_1$ . 35,000 ohms, 10 watts
- $R_2$ . 5000 ohms, 10 watts with adjustable tap
- $R_3$ . 2 megohms
- $R_4$ . 50,000 ohms
- $R_5$ . 100,000-ohm potentiometer
- $R_6$ . 200,000 ohms



operating the 6L6 tube very close to its cutoff, and better regulation will be secured by introducing an additional bleeder, or reducing the resistance of  $R_4$ ,  $R_5$ ,  $R_6$ . The output voltage may be reduced to about 135 volts by adjusting  $R_5$ , while for small currents the maximum voltage is about 400.

A power transformer with a rating of 200 milliamperes or more should be chosen to assure a low voltage drop. A voltage output greater than 550 is permissible if  $R_1$  is increased to limit the current through it to about 10 milliamperes; rectifier tubes of higher voltage rating than the 83 should probably also be substituted in such a case.

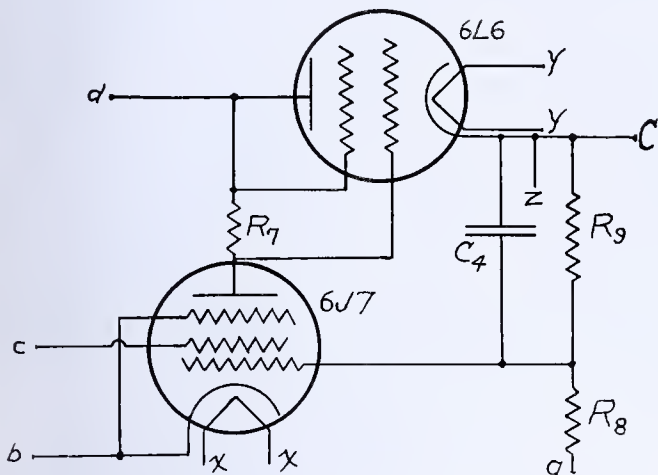


FIGURE 2. SUPPLEMENTARY CIRCUIT

- C. [Output, controlled with respect to A (Figure 1), so that the voltage between C and B may be adjusted to any value from zero to about 200 volts]
- C<sub>4</sub>. Paper condenser, 2 mfd.
- R<sub>7</sub>. 2 megohms
- R<sub>8</sub>. 1500 ohms, 10 watts
- R<sub>9</sub>. 2250 ohms, 10 watts

If it is preferred to use a type 874 voltage-regulator tube instead of the neon glow lamp,  $N_1$ , the resistance in series should be reduced to give a current of about 15 milliamperes, and  $R_4$  and  $R_5$  changed to 75,000 ohms each. The minimum voltage obtainable will be increased about 30 volts. It is ordinarily better to eliminate  $N_2$  altogether than to use a type 874 tube in place of it.

The 6L6 tube was chosen because the power transformer used was supplied with 6.3-volt filament windings, and the separate cathode of the 6L6 tube allows the output tube of the supplementary circuit for low voltages (Figure 2) to operate from the same filament winding. Type 2A3 is more frequently used, and will pass up to about 75 milliamperes with slightly less voltage drop. For greater output than this, the 6L6 has a slight advantage, and its indirectly heated cathode has a decided advantage if it is essential to filter out as much alternating current hum as possible. The 6J7 was chosen to match the metal 6L6, but a 6C6 would give identical results.

For most purposes it is merely necessary to connect the screen of the 6J7 to such a point on  $R_2$  as to give a voltage between 90 and 100 volts above the cathode, and if preferred,  $R_2$  may be a fixed resistor of 4000 ohms and the screen connected between it and  $R_1$ . However, if especially accurate regulation is necessary, the voltage control should be put into operation with its load connected, and the screen voltage adjusted until artificial changes in input voltage cause no change in output voltage. It will be necessary to provide a very sensitive means of detecting changes in the output voltage. In this laboratory, the adjustment has been made so that an increase or decrease of 15 volts in the input voltage changes the output less than 1 millivolt, the smallest change which the author could detect. For this accuracy, filter condensers

$C_1$  and  $C_2$  should be at least 8 microfarads each. If the special conditions of the circuit require for this adjustment a screen voltage much above 100 volts, tube  $N_2$  should be omitted,  $R_2$  increased to about 10,000 ohms, and the screen voltage adjusted as outlined above. If the screen voltage is too high, output voltage will drop on increase of input voltage, and vice versa.

The circuit as shown is designed to correct accurately for line voltage changes at a fairly constant output current drain; a 20-milliamper increase in output drain may cause a 20-millivolt voltage drop. This can usually be corrected by replacing  $N_2$  by a 5000-ohm resistor, and increasing the resistance of  $L_1$  and  $L_2$  or introducing a series resistor of 500 to 1000 ohms immediately before or after  $L_1$ . It will also be better to use a type 5Z3 tube instead of the 83V, or two type 81 tubes if it is necessary to use a transformer of higher voltage to produce the necessary output voltage. With these changes, an increase in output drain will lower the screen voltage of the 6J7 and thus tend to hold the output voltage constant. If this compensation is not sufficient for the requirements, the screen of the 6J7 should be connected to a separate bleeder between the negative line and the plate of the 6L6, which may consist of a 100,000-ohm resistor connected to the negative line, a 100,000-ohm potentiometer for screen voltage adjustment, and a 300,000-ohm resistor connecting this to the positive line. Such a circuit can be adjusted to hold the output voltage constant within less than 1 millivolt with a change in drain of 50 milliamperes, but there will be some over-compensation for changes in line voltage. This will usually not be more than 2 to 4 millivolts for each volt change in line voltage.

If an electronic voltage control is to supply current to a device that will be damaged by a brief over-voltage, a switch should be provided to delay the application of voltage after turning on the apparatus until the cathode of the control tube has had time to heat to operating temperature. This is especially important when a 2A3 output tube is used, as it will pass current for some time before a 6J7 or 6C6 warms up sufficiently to control the voltage.

Low Voltages

The lowest voltage obtainable from a circuit of the type just described is ordinarily from about 90 to 140 volts, depending on the voltage delivered from the rectifier and the current drawn from the output. A lower voltage may be obtained by means of a voltage divider if the current required is constant, but such a device is useless if the drain fluctuates, and if more than a few milliamperes are required temperature changes in the resistors may lead to troublesome voltage changes. But if the circuit shown in Figure 2 is connected to Figure 1 at the indicated points,  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $x$ ,  $y$ ,  $z$ , the voltage between C and B can be adjusted to any value from zero to about 200 volts, which is well above the minimum available without this addition. The bleeder,  $R_8R_9$ , carries sufficient current to allow a drain up to 30 milliamperes between C and B; if a larger current is required, an additional bleeder may be connected from A to C to permit an output up to about 175 milliamperes.

If the voltage control is to be used both with and without the supplementary circuit, the latter should be supplied with a switch to disconnect its filaments and its plate connection at  $d$ .

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# An Electronic Recording Analytical Balance

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IN THE course of photoelectric studies on the properties of fine suspensions, certain optical difficulties indicated the desirability of supplementing the optical measurements with sedimentation data on the same system. Recording balances for this purpose have been devised, notably by Oden (2, 4) and Svedberg and Rinde (5). Many other problems, such as studies on desiccants, rate of reaction, etc., may be solved most conveniently with an instrument of this type. While the groundwork (1) has been laid for this problem, the extraordinary progress in electronics has provided means for an entirely new and improved solution.

The original instrument which was developed about a year ago (demonstrated at the meeting of the New York Section of the AMERICAN CHEMICAL SOCIETY, December 10, 1936, 3) consisted of a standard chainomatic balance in which the

chain mechanism was driven by a motor. A small target mounted on the balance pointer intercepted a sharply focused beam of light. A conventional photocell amplifier system operated a set of relays controlling the restoring motor. The balance was therefore continuously maintained in the balanced equilibrium condition, without any mechanical contacting of the system. The position of the chain was recorded by means of a contactor mounted on the chain block, which traveled over a slide wire. The potential drop along this slide wire was measured by a standard recording potentiometer. This instrument functioned satisfactorily, but certain obvious limitations suggested an improved design: The instrument would function in one direction only—i. e., a gain or loss in weight—sudden demands on the system could not be accommodated, and the relay system might become temperamental and require frequent adjustment. During the past year the authors have completely redesigned the system, and the present paper describes the improved instrument which possesses the following characteristics:

1. No mechanical or electrical contacting of the beam.
2. Rate of compensation proportional to the demand.
3. "Antihunting" circuit to prevent overshooting and tendency to oscillate about the equilibrium position.
4. Directional discrimination. The balance will respond instantly to an increase or decrease in weight without hesitation or "nervousness."
5. The recording is linear and direct-reading, requiring no extended computation from the record.
6. The time axis is linear and accuracy is assured, as the recorder is driven by a synchronous motor and will therefore record time as accurately as a Telechron clock. A choice of speeds is available.
7. The sensitivity is adjustable, so that one division on the record may be set at exactly 10, 1, or 0.1 mg. This is an electrical adjustment and necessitates no mechanical adjustment of the balance proper.
8. The over-all sensitivity is from 20 to 50 times greater than the normal sensitivity of the balance proper, owing to the very precise photoelectric scanning of the pointer since 0.04-mm. displacement of the latter is sufficient to energize the compensating motor.
9. Remote indication and automatic control are inherent features.
10. The instrument utilizes standard components—i. e. a magnetically damped chainomatic balance, a recording potentiometer, and readily available electronic parts. No elaborate mechanical or instrumental construction is involved.

A general view of the instrument is given in Figure 1. A standard relay rack provides the framework, the upper portion of which supports the balance. Below this is located the restoring motor. The remaining space is occupied by the recording-potentiometer amplifier and associated equipment.

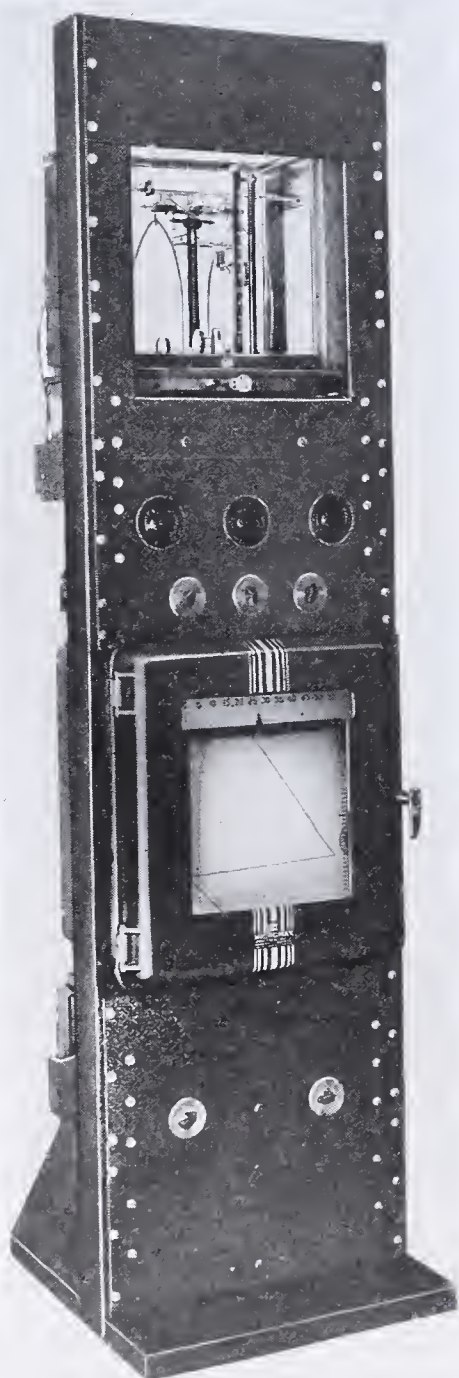


FIGURE 1

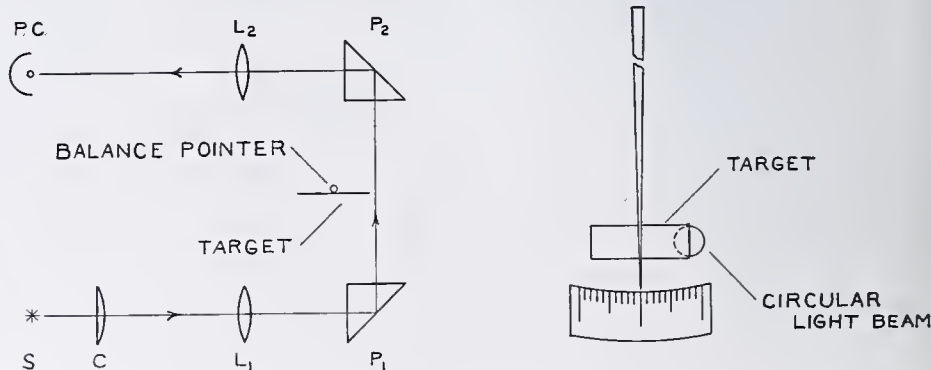


FIGURE 2







intercepted beam, the photocurrent flowing through  $R_6$  will drive the grid of the upper 89 toward positive potentials.  $R_5$  is adjusted to compensate for this until the plate current is equal to that of the lower 89. Since transformer  $T_1$  applies an additional but alternating potential to the plates of both tubes, under this balanced condition the symmetrical pulsations in the two primary windings of transformer  $T_2$  cancel and no potential appears at the secondary terminals. If now the light intensity at  $P$  increases or decreases, the plate current of either the upper or lower 89 predominates and cancellation in the primary of  $T_2$  no longer occurs; consequently a potential will appear at the secondary of  $T_2$  proportional to the change in light intensity and either in phase or  $180^\circ$  out of phase with the secondary potential of  $T_1$ . This photocell circuit which scans the balance pointer and decides the magnitude and direction of the required compensation is the electronic equivalent of a rheostat and reversing switch.

The potentials appearing across the secondary of  $T_2$  must be amplified before they are applied to the gas tubes which drive the motor. The 6J7 and two 6C5 tubes constitute an audiofrequency amplifier designed for efficient operation at 60 cycles. A high-quality public address amplifier would function appropriately in place of this unit. The voltage gain is about 45 decibels ( $35,000\times$ ) and is controlled by  $R_{11}$ . This follows current practice in high-quality amplifiers, in which the gain control is placed between the first and second stage. The last 6C5 tube controls the grids of the gas triodes through the class B transformer,  $T_3$ . The gas-triode grids are biased by battery  $B_4$ , and grid resistors  $R_{13}$  and  $R_{19}$  limit grid currents which might arise from strong signals. Plate potentials are supplied by transformer  $T_4$  through the motor armature and either half of the split-field winding. The direction of rotation therefore depends upon which of the two tubes fires, and this in turn depends upon the phase relationship of the incoming signal, as described above. With the balance in true equilibrium, no signal arises, and the motor is at rest.

The motor,  $M_1$ , is mechanically coupled to the chain-restoring mechanism through the 8 to 1 reduction gear, R. G. It is also coupled to the shaft of motor  $M_2$  which acts as a generator and antihunting regulator. The field of this generator is excited by battery  $B_3$ . The potential developed by the generator is applied

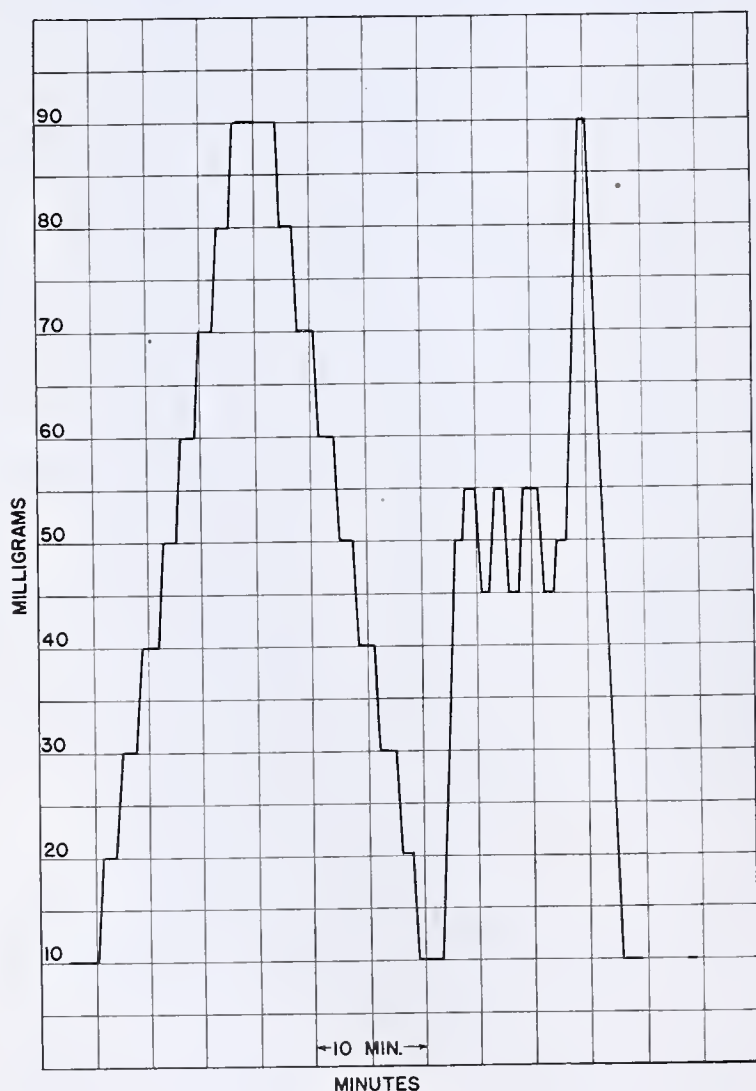


FIGURE 4

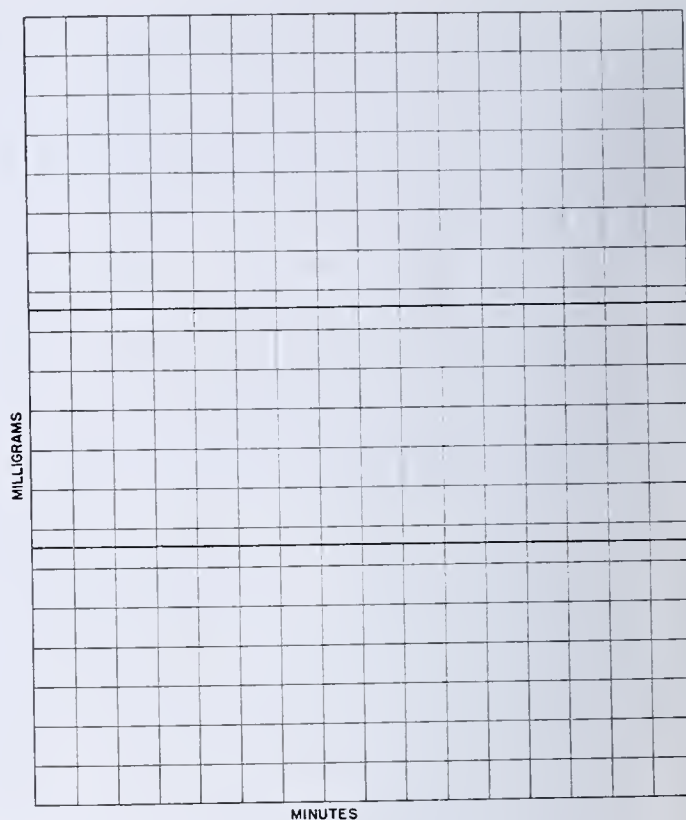


FIGURE 5

as additional bias to the lower 89 type tube and tends to counteract the off-balance signal. The magnitude of this compensation can be controlled by  $R_2$ . When sudden, large demands are made upon the system, motor  $M_1$  races in the appropriate direction to effect rebalancing. Under these conditions the potential delivered by  $M_2$  is small compared with the unbalanced signal, and  $M_1$  retains its high speed. As the equilibrium position is approached, the effect of  $M_2$  becomes an appreciable fraction of the signal, and the speed of  $M_1$  is reduced. In the immediate vicinity of equilibrium the motor exhibits a "fluttering" action and overshooting does not occur.

The chain-restoring mechanism is shown in the lower left. The helical feed screw supplied with the balance was replaced by one with smaller pitch—i. e., 20 threads per 2.5 cm. (1 inch). The block driven by this screw carries a hook for the free end of the chain and also a sliding contact moving over the uniform slide wire,  $R_{21}$ .

The position of this block, which carries the conventional vernier, establishes the instantaneous value of the weight of the sample. To record this and subsequent positions, the sliding contact picks off potentials from the slide wire which is fed by battery  $B_5$  and network  $R_{22}$ ,  $R_{23}$ , and  $R_{24}$ . The voltage divider,  $R_{22}$ , has two functions: It is equivalent to the end coils of a Kohlrausch slide wire and eliminates uncertainties in the exact positioning of the extremities of the wire, and it enables one to adjust the resistance of the network to the critical external damping resistance required by the recorder galvanometer.

The power supply shown in the lower right (Figure 3) requires no particular explanation, as it follows standard practice. Line fuses are included for protection and red and green pilot lamps (not shown in the circuit) are used to indicate filament and plate excitation of the gas triodes. The controls which appear on the panels (Figure 1) are those necessary for initial adjustment and operation. They include in addition to the switches and pilot lamps detector-discriminator-unit controls  $R_3$ ,  $R_5$ ; antihunting control  $R_4$ ; amplifier gain control  $R_{11}$ ; and recorder network  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$  (for adjusting scale weights on recorder paper).

It has also been found convenient to include pilot lamps in the field circuit of  $M_1$ . These are located on the panel immediately under the balance case. The continuous "blinking" of either lamp indicates the direction of compensation which is taking place, no matter how small it may be.

The use of batteries may be considered objectionable, since in the main the instrument is operated from the power line. However, with the exception of  $B_3$  which is not at all critical, all batteries deliver negligible current and their life is practically equal to the shelf life. Furthermore, the stability and reproducibility of the balance are in no wise affected by the potential of these batteries, with the possible exception of  $B_5$ . With little



additional difficulty this may be checked automatically from time to time, just as the working cell of the recorder is periodically monitored.

To those unfamiliar with electronic circuits, the arrangement may seem very complex. Aside from the detector discriminator unit, which is new, standard practice is followed and any circuit expert would understand it at a glance.

The recorder is a Leeds and Northrup Micro-max Model S. One division on the recording paper is equivalent to 0.1, 1.0, or 10 mg.

Calibration

The performance of the recording balance is illustrated in Figure 4. In this case, carefully adjusted 10-mg. loads were placed on the pan and the balance was permitted to re-adjust itself and record the value. Successive 10-mg. loads were added up to a total of 90 mg., then removed progressively, and finally a single weight was alternately added and removed as shown on the right side of Figure 4. The maximum recorded deviations are of the order of 0.1 mg. This is a limitation imposed by the recorder and not a measure of the maximum precision of the automatic balancing, as is shown below. Figure 5 shows stability records at two constant loads. Over very long periods (days) the recorded values may show a drift which indicates the necessity of rebalancing the net-work,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$ , just as in standard potentiometer practice. The balancing system, however, is not subject to such fluctuations and will remain balanced indefinitely. This, of course, assumes the absence of gross thermal disturbances of the balance proper.

Reproducibility and Sensitivity

The precision of recording is limited by the total space covered on the record and the exactness of rebalancing greatly exceeds that which can be recorded conveniently. Successive automatic weighings of an approximately 20-gram load (20.050 grams) were as follows: 20.0500<sub>5</sub>, 20.0500<sub>0</sub>, 20.0501<sub>0</sub>, 20.0500<sub>5</sub>, 20.0500<sub>5</sub>, and 20.0500<sub>0</sub>. In this series of measurements, the balance was thrown off balance and allowed to readjust itself. When automatic compensation was completed, the weight was read from the column and accompanying vernier. No differences that could be estimated on the vernier could be detected. The sensitivity is therefore about  $\pm 50$  micrograms for a 20-gram load. Simple calculation showed that a 0.02-mm. displacement of the pointer would suffice to start the compensating motor. The high sensitivity is therefore due to the very delicate scanning system. No claim is made for the absolute value of the weights listed as it was of no interest at this point.

Accuracy

It is obvious that the high reproducibility and sensitivity will have little to do with the accuracy of weighing, which will be governed by the reliability of the chain. Indeed this is the present limitation. It is always possible to calibrate the chain with artificial standards and apply empirical corrections. With more difficulty the chain may be adjusted bit by bit until it is uniform. Either procedure is entirely unnecessary if one is content with ordinary sensitivity and accuracy, but where inordinate sensitivity is available it becomes of interest to see from what direction further improvements must

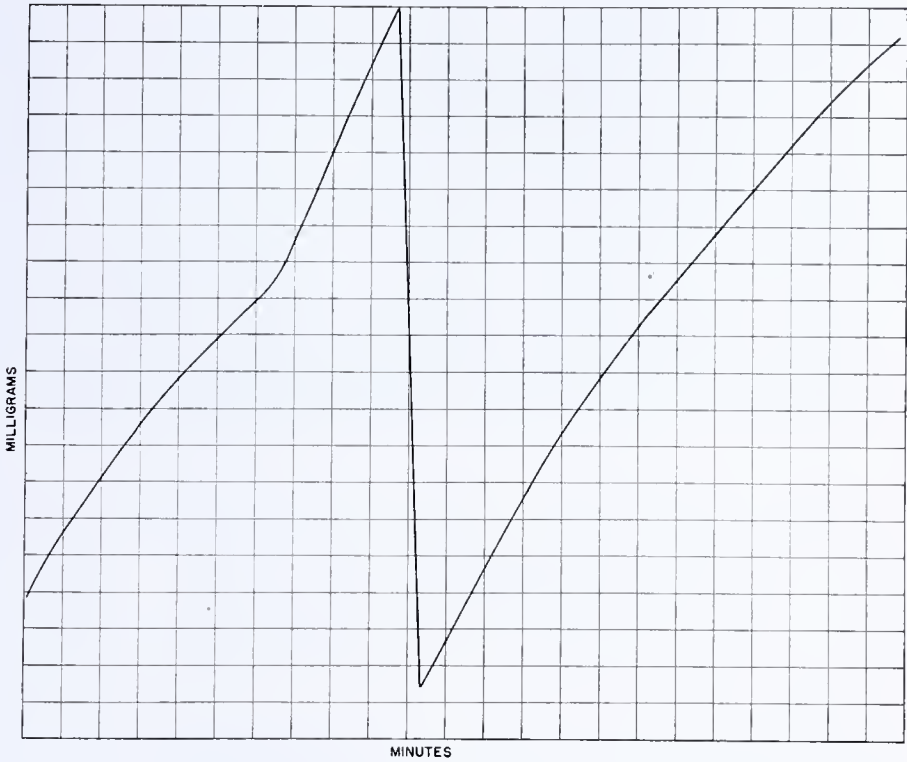


FIGURE 6

come. With all the limitations of present-day chains, they are probably preferable to electromagnetic balancing schemes where an empirical relationship between current and weight is practically mandatory.

Stability

The stability is independent of the small fluctuations in the light source (constant-current transformer). The question of vibration arises naturally, since motors are mounted in the assembly. Although these are mounted on sponge rubber bases, there is a very faint but perceptible tremor in the system. Careful investigation of this point has led to the conclusion that these high-frequency, symmetrical tremors are in no wise objectionable but may possibly contribute to the establishment of a "dynamic" equilibrium. Gross asymmetric shocks, occasioned by heavy vehicles or the slamming of doors, are of course as detrimental here as with any sensitive balance.

Line voltage variations have no influence on stability and can only cause changes in sensitivity and speed of response. Inasmuch as both factors are far in excess of requirements, such effects are negligible.

Range

With the present arrangement, weight changes of  $\pm 100$  mg. can be accommodated without manual attention. The range can be extended by the use of a heavier chain with little sacrifice in sensitivity. When changes greater than 100 mg. are encountered an additional 100-mg. weight can be placed on the pan; the chain block will race to the zero position and then resume its normal course. This is illustrated in Figure 6, in which a particularly rapid weight increase is recorded. An automatic mechanism may be provided to release 100-mg. weights as required (1, 4).

Summary

An electronic recording analytical balance is described which is direct-reading, rapid, and sensitive. All mechanical or electrical contactors, relays, and the like have been



eliminated by substituting inertia- and lag-free electronic methods. No elaborate mechanical construction is involved, as standard parts are used throughout. It should be of general utility in all investigations involving very slow or very rapid changes of weight or in the study of phenomena which can be followed indirectly by a change of weight. The complete instrument costs about \$500, excluding labor.

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## Antifoaming Device for Use in Concentration of Noninflammable Liquors

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THE prevention of foaming is generally accomplished by the addition of an antifoaming agent such as kerosene, capryl alcohol, etc., or by the use of mechanical devices, among which are an air jet (2, 3, 4, 6, 7), a special still-head (1), and a paddle wheel (5, 8).

The investigation of some alkaline pulping liquors, in this laboratory, necessitated their concentration by distillation. These liquors foamed profusely. The commonly used antifoaming agents were unsatisfactory because they were inefficient, their presence interfered with subsequent chemical examination of the residue, and the volatile agents were lost by distillation. Fanto (2) used a current of cool inert gas to break the bubbles by condensation of the enclosed vapor, but stated that sometimes the liquid was carried over mechanically, so that it was necessary to redistill.

Certain evaporators of commercial size control foaming by

continuing the heating surfaces above the liquor level, thus destroying the foam by contacting and vaporizing the liquid film (9). An improvement on this action is made use of in the apparatus shown in Figure 1, whereby the heat from the coil, A, disrupts the foam bubbles without contact and allows the distillation to proceed at a rapid rate without carry-over.

### Apparatus and Operation

The assembled apparatus is shown in Figure 1. The foam-breaking coil, A, consists of 88 cm. of No. 22 gage (0.64-mm.) Nichrome wire, in the form of a helix, fastened to No. 16 gage (1.3-mm.) copper wire leads, B and B'. The leads pass through the stopper, D. Coil A must be placed low enough to avoid undue heating of the flask wall above it. The power is 110-volt alternating current, suitably controlled by a resistance unit or transformer.

The resistance unit used is made by connecting two 500-watt heating coils, C and C', mounted in porcelain sockets, with switches, S and S', so that one or both may be used. Switch S' controls the unit. The temperature of coil A is higher when switch S is closed than when it is open. The binding posts, E and E', are convenient for connecting the copper leads, B and B'. Material for the unit costs about one dollar.

Flask F should have a capacity of 2 liters or more, providing sufficient room to place the hot wire, A, at least 4 cm. from the glass above it. The liquid should be heated to incipient boiling before the current is turned on. Ordinarily, only coil C is used as the wire, A, need not be at red heat. However, the wire should be hot enough so that the bubbles burst at least 1 cm. from the wire, in order to prevent the wire from becoming coated by material which would then dry and burn. The temperature of wire A may be varied by changing its length or gage, or by changing the resistance of the coils, C and C'. Condensate from tube T should not drop on the hot wire. Once started, the distillation proceeds at a rapid rate without further attention.

### Discussion and Conclusions

The antifoaming device described is limited in use to the distillation of noninflammable substances. It has proved successful in the laboratory distillation and concentration of alkaline pulping liquors that foam excessively and should prove useful in the distillation of many aqueous foam-producing solutions. There appears to be no reason why it should not be applicable to large-scale apparatus.

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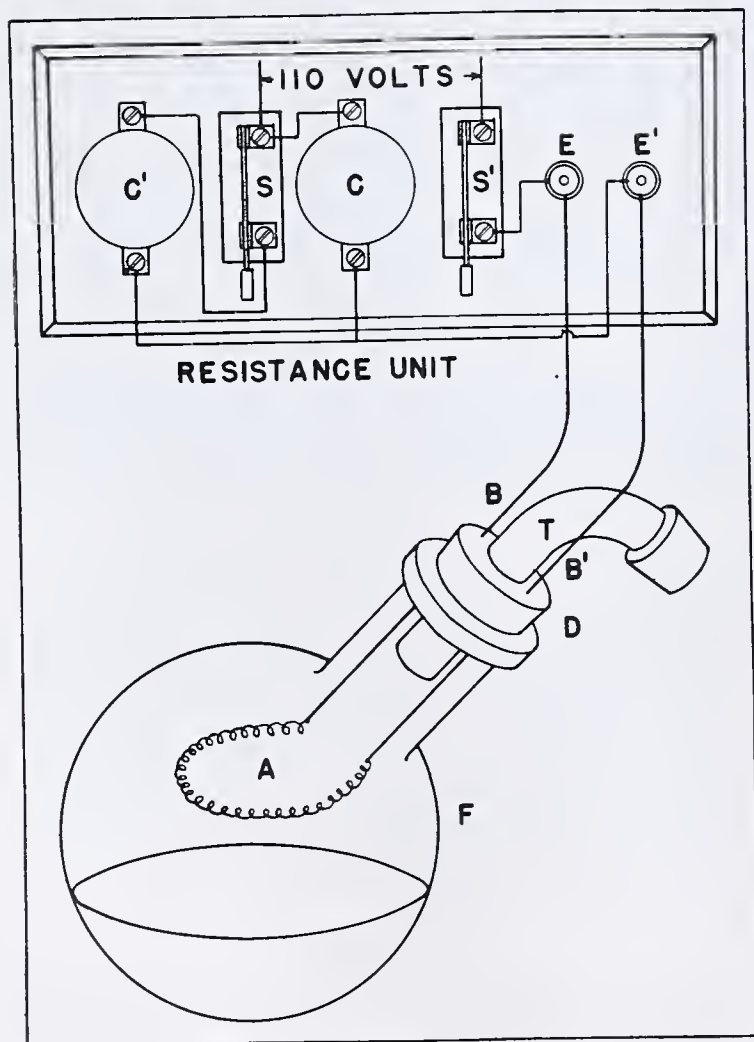


FIGURE 1. DIAGRAM OF APPARATUS





## Thomas and Hochwalt Laboratories, Research Division of Monsanto Chemical Company

MARY B. MOSHIER, Thomas and Hochwalt Laboratories, Dayton, Ohio

THE Thomas and Hochwalt Laboratories, a Research Division of the Monsanto Chemical Company, is an ideally situated and well-planned unit at the outskirts of Dayton, Ohio. The quiet, almost rural setting, free of the distractions usually coincident with urban or industrial surroundings, is an excellent site for a chemical research laboratory. The main part of the building was erected in 1929 as the then new home of the Thomas and Hochwalt Laboratories, Incorporated. It was designed by Coles and Coleen, architects of Chicago. In 1936, upon the merger of the laboratories with the Monsanto Chemical Company, a harmonious addition was made to the building under the supervision of Douglas Lorenz, a Dayton, Ohio, architect.

### The Main Building

The structure, including the added wing, provides 12,200 square feet of floor space. The front section, comprising air-conditioned, sound-proofed offices and library, is of two stories. The remainder of the building is a one-story, L-shaped structure which houses fourteen laboratories, an instrument room, an office for chemists, a sample room, a stock room, a wash room for apparatus, locker room, dining room, and kitchen. The latter, together with the dining room, is

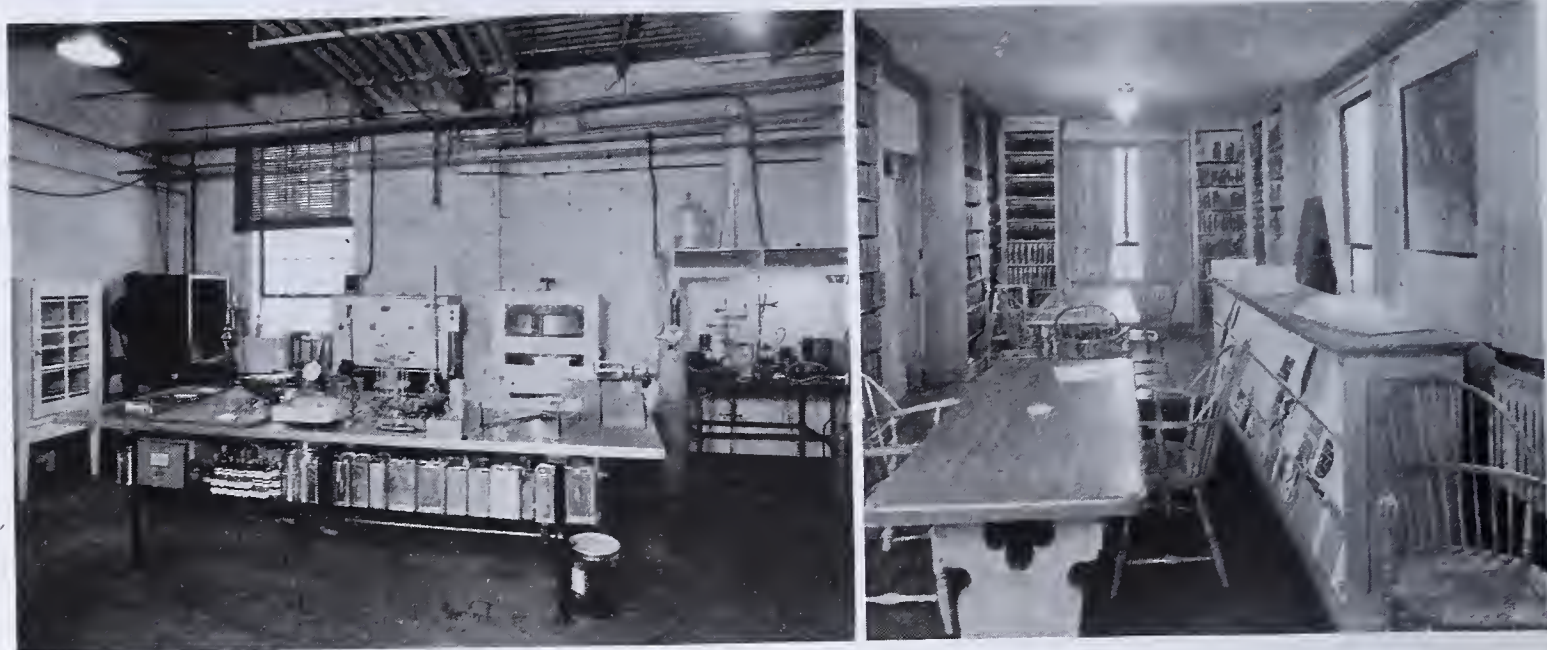
located at the end of the new addition, thus providing for outside accessibility to the kitchen and for quiet seclusion of the dining room. Corridors placed between the administrative section and the laboratories, and between the new wing of the laboratory and the old section, diminish extensive fire hazard.

As can be seen in the accompanying layout of the plant, the floor space afforded by each laboratory is somewhat varied. Such variation is desirable in a research laboratory where the type of problem determines the space required for its execution. As a rule, not more than two men are assigned to each laboratory; generally, these two men work on the same problem. Although each laboratory is provided with desks, the chemists' office and the library afford additional privacy. The spaciousness of each laboratory makes possible the retention of assembled apparatus from one job to another. Except in two large laboratories, the benches are arranged around the sides of each room in order to prevent possible obstruction of light. Treatment of the tops of the benches with an acid-proof stain has been found to give satisfactory protection against chemicals. The use of wood tops instead of a harder surface has also been found to cut down on breakage of glassware.

Although the entire plant is equipped with a sprinkler sys-







COATINGS LABORATORY AND LIBRARY

tem, each laboratory is provided with a shower placed over sinks, as a further safety measure against fire or chemical injury. Fume hoods are found in each laboratory. Because the fan for each hood is mounted on the roof of the building, quietness in operation is attained. Whenever possible, additional precautions against poisonous gases are taken—for instance, in several of the laboratories the Mine Safety Appliance carbon monoxide alarm is used.

Each laboratory is an individual unit, fitted with the necessary equipment to carry on research of a specific nature. Ample closet and shelving space enables the storing of each man's apparatus and supplies within his own laboratory. Sinks are plentifully supplied, but washing of all apparatus and equipment is done in the centrally located washroom by a man employed for that purpose.

Since Monsanto's interests are broad, the type of research carried on necessitates almost every type of chemical equipment and apparatus. Balances and other equipment which require special care, such as gas-analysis apparatus, Podbielniak fractionating columns, constant-temperature baths, and pH determination outfits are kept in the instrument room. Instruments used for the evaluation of special compounds are found in the materials-testing laboratories.

Except in a few cases, however, the evaluation of materials synthesized in the laboratories is not conducted at the Dayton unit. The greater part of the work deals with organic and inorganic synthesis in the laboratory and its application and control in pilot-plant work. Hence in most laboratories is found that type of equipment which is generally associated with research in synthesis. The study of gaseous reactions, necessitating the use of rheostats for controlling the temperature of the reaction chamber, flowmeters, thermocouple switches, and wash towers, for instance, is conducted in one of the laboratories; another laboratory is equipped for high-



AERIAL VIEW OF LABORATORIES

pressure work. Equipment for the study of thermal conditions of reactions—for example, calorimetric determinations of heats of reactions—is provided for in the analytical laboratory, where is also found other apparatus used in determining data necessary for the elucidation and control of organic and inorganic reactions.

### The Library

Since chemists at the laboratories realize that adequate chemical literature is as important as is equipment and other working facilities, the library at the laboratories has been carefully fostered. Begun by Charles A. Thomas and Carroll A. Hochwalt some twelve years ago, it has had a phenomenal growth and now carries a current subscription list of some eighty American and European chemical journals. Although housing facilities do not permit the binding of each journal, all are kept on file in steel stacks in a room especially designated for that purpose. A great many of the more important journals are bound, however, and complete files of these, including the American, British, and German abstracting journals, are in the library. An especially designed magazine rack is used for the current journals. Besides indispensable reference literature like Beilstein, Landolt-Bornstein,





PILOT PLANT, CORRIDOR, AND TWO LABORATORIES

Richter, Mellor, etc., there is a good collection of monographs and publications on fields of especial interest. A file of catalogs and technical literature is kept in the library as well as an extensive file of American and foreign patents.

### The Dining Room and Kitchen

Because the laboratories are not located in an industrial section of the city, a dining room and kitchen were deemed indispensable and were accordingly incorporated into the new addition to the building. The dining room accommodates sixty people. A decorative scheme has been carried throughout, and it is air-conditioned and sound-proofed. All kitchen equipment is of stainless steel.

### The Pilot Plants

Besides the main structure, three smaller buildings afford facilities for pilot-plant work and materials testing. With due regard to fire protection these are spaced at least 100 feet apart from the main building and from each other. They provide a total of 8800 square feet of additional floor space. Here are found units for studying vapor-phase reactions and a unit for studying gaseous reactions at high pressure. Opportunity is given for the study of other reactions on a pilot-

plant scale. Electrically operated controls are used as are automatic temperature controls, indicating thermocouples, and precision gas meters. A 2200- to 220-volt transformer ensures ample power for the operation of the pilot plants. Here, too, are found such auxiliary equipment as assay furnaces and small gas muffles and electric muffles, allowing a wide range of temperature control. An optical pyrometer is used for measuring the temperatures of these furnaces. For large-scale fractionation, there is a twenty-plate column of approximately 20-gallon capacity. Similarly, in the protective coatings laboratory, housed in a separate building, is found such apparatus as temperature baking ovens, spray booths, grinding mills, kettles, weatherometer, and other equipment which is ordinarily found in laboratories of this kind. Provision is made for local exposure of panels on roofs.

### The Machine Shop

It has been found that very often a novel piece of equipment needed can best be made to specifications in the laboratories. For this reason, one of the smaller buildings houses a machine shop which is in charge of an able mechanic who is constantly kept busy at making some piece of laboratory or pilot-plant equipment designed by a chemist. Although harkening back to old "glass-blowing" days, the laboratory machine shop has.



TABLE II. REFRACTIVE INDEX OF SATURATED AQUEOUS SOLUTIONS

Substance	Pure Substance	Saturated Solution	Water	$\Delta n_D$	Solubility of Substance in 100 Parts of H <sub>2</sub> O
Quinoline	1.6283	1.3345	1.3325	0.0020	Slightly soluble
<i>o</i> -Toluidine	1.5728	1.3350	1.3325	0.0025	1.5
Ethyl ether	1.3515	1.3355	1.3325	0.0030	7.5
Methyl alcohol	1.3288	1.3288	1.3325	0.0037	$\infty$

TABLE III. SENSITIVITY OF SCHLIEN DETECTION

Substance	$\Delta n_D^a$	Schlieren
Quinoline	0.0020	—
<i>o</i> -Toluidine	0.0025	—
Ethyl ether	0.0030	+
Methyl alcohol	0.0037	+
Sucrose (aqueous solution)	0.0020	Very faint
Sucrose (aqueous solution)	0.0011	—
Hydroquinone (aqueous solution)	0.0050	+
$\alpha$ -Naphthylamine (aqueous solution)	0.0025	Very faint

<sup>a</sup>  $\Delta n_D$  is the difference in refractive index of the fluid and static samples.

The two procedures found applicable by the authors are the capillary and the *schlieren* methods.

### Capillary Method

This method was described in the first paper at this series (2). In the case of solids it has been found advisable to determine at once whether or not the substance is soluble in the maximum amount of solvent permissible under the definition of what constitutes "soluble" without determining the exact solvent-solute ratio of a saturated solution. That is, the sample of the substance was weighed out in the capillary and then 25 times as much solvent was added. If a residue remained after mixing, the substance was designated as "insoluble," if none remained undissolved, "soluble." Although the volume of the solid cannot be determined by the length of solid layer in the capillary, a diminution in the volume on adding additional solvent can be determined accurately. Results obtained using this method are given in Tables I and IA.

The capillary method is recommended for all determinations in which a semiquantitative result is desired. For very rapid determinations of solubility in which the analyst wishes to know only whether the substance is soluble according to the definition of Kamm (4)—i. e., 1 part in 25 parts of the solvent—the *schlieren* method is to be preferred. The technic has been modified considerably from that described previously (2) and hence will be given in detail.

### Schlieren Method

The appearance of *schlieren* depends upon the fact that the fluid and static samples (1) differ in refractive index. If, as in this case, the samples differ by the presence of the solute in one, the appearance of *schlieren* will depend on the degree to which the amount of solute will change the refractive index of the solvent. If refractivity is regarded as an additive property, the change in refractive index will depend on two

factors: (1) the difference in the refractive indices of the solvent and the solute; and (2) the concentration of the solute. Theoretically, therefore, the appearance of *schlieren* should not be a measure only of the concentration of the solute. The following experiments show, however, that within certain limits *schlieren* can be used as a direct measure of solubility.

Several compounds with a high refractive index and a solubility in water below the limit solubility set by Kamm (4)—that is, 4 per cent—were selected. Solutions of these compounds might be expected to differ sufficiently in refractive index from that of the pure solvent to give *schlieren* despite their low solubility. Several other compounds with a refractive index very close to that of water but with a solubility above the limit were also used. These would not be expected to give *schlieren* unless in very high concentrations. The refractive index at 18° C. of saturated solutions of all these substances was determined by means of an Abbe refractometer. The results are shown in Table II.

From Table II it is evident that if a method of observing *schlieren* which is sensitive to differences of refractive index of not less than 0.0025 is used, it should be possible to distinguish between "soluble" and "insoluble" substances by the use of *schlieren*.

In order to reduce the sensitivity of *schlieren* detection to this value, the usual "*schlieren* microscope" or the "visual method" of Emich (1) cannot be used. Emich states that the sensitivity of the microscope method of observation is  $\Delta n_D$  0.00005 and that of the visual method,  $\Delta n_D$  0.0001. He also suggested the use of test tubes with a reduction in sensitivity to  $\Delta n_D$  0.0005. The authors have found by experiment that if a simple glass tube 4 mm. in inside diameter, 6 mm. in outside diameter, and about 60 mm. long sealed at one end, is used in place of the usual *schlieren* cell or the one mentioned in the first paper of this series (2) and the method of illumination is changed (discussed later), the sensitivity of the *schlieren* observation is reduced to the desired value. Results of some experiments in which water was used as solvent are shown in Table III.

TECHNIC FOR LIQUIDS. The substance to be tested is used as the fluid sample. The *schlieren* tube is filled with the solvent to

TABLE IV. SOLUBILITY OF ORGANIC SUBSTANCES

Substance	H <sub>2</sub> O	Ether	5% HCl	5% HaOH	H <sub>2</sub> SO <sub>4</sub>	Solubility Schlieren method	Group Kamm's method
Solids							
Anthranilic acid	—	+++	+++	+++	..	III	III or IV
Acetanilide	—	++	(+?)	—	..	VII	VII
Benzoic acid	—	++	..	+++	..	IV	IV
Benzidine	—	++	+++	—	..	III	III
$\beta$ -Naphthol	—	+++	—	+++	..	IV	IV
Phthalimide	—	+	—	+++	..	IV	IV
Phenol	+++	++	+++	+++	..	I	I or III
Sodium benzenesulfonate	+++	—	+++	+++	..	II	II
Sucrose	+++	—	+++	+++	..	II	II
Resorcinol	+++	++	++	+++	..	I	I
Trinitrotoluene	—	+	—	++	..	IV	IV
Uric acid	—	—	—	++	..	IV	IV
Liquids							
Ethyl acetate	++	+++	+	—	++	I or V	I or V
Ligroin (b. p. 90–120°)	—	+++	—	—	—	VI	VI
Acetic anhydride	+++	++	+	+++	..	I	I
Ethyl ether	+	—	(+?)	—	++	I or V	I or V
Aniline	(+?)	+++	+++	—	..	III	III
Dimethylaniline	—	+++	+++	—	..	III	III
Quinoline	—	+++	+++	—	..	III	III
Ethyl alcohol	+++	+	++	+++	..	I	I
Glycerol	+++	—	+++	++	..	II	II
Benzyl alcohol	—	+++	—	—	Ppt.	V	V
Nitrobenzene	—	+++	—	—	..	VII	VII
Acetophenone	—	+++	—	—	++	V	V
Acetone	+++	++	++	++	..	I	I
Acetic acid	+++	+	+++	+++	..	I	I
Toluene	—	+++	—	—	—	VI	VI
Ethyl bromide	—	+++	—	—	—	VI	VI

— No *schlieren*.

(+?) Very faint *schlieren* (regarded as negative).

+, ++, +++ *Schlieren* observed.



serve as the static sample. The fluid sample is drawn into a capillary pipet varying in diameter from 0.5 to 1.0 mm. The more viscous the substance, the wider the capillary pipet should be. The *schlieren* tube is held so that the illumination is obliquely downwards, as obtained, for example, by holding the tube below the (horizontal) edge of a lamp shade, or below a horizontal crossbar of a window. The illumination should not be too intense. When only very small amounts of substance are available, the fluid sample may be introduced, as suggested to the authors by A. A. Benedetti-Pichler, into the static sample by first absorbing it in a very small piece of porous tile which has been fixed in a platinum wire and then dipping the tile into the static sample. In the case of inert solvents such as water or ether, a piece of ashless filter paper may also be used.

**TECHNIC FOR SOLIDS.** A saturated solution of the solid substance is first prepared by placing a drop of the solvent in a depression of a spot plate and adding the solid until some remains undissolved. In the case of solvents which are pure substances, a saturated solution may also be prepared by making up a solution on the spot plate and allowing it to evaporate until a crust forms. The clear solution is taken up in a capillary pipet and used as the fluid sample. In the case of solvents which are already solutions, such as 5 per cent hydrochloric acid and potassium hydroxide, a control consisting of several large drops of the solvent is placed in an adjacent depression of the spot plate and is allowed to stand until the fluid sample has been taken up in the pipet. Then the control is used as static sample. In this way differences in refractive index between the static and fluid samples which might result from partial evaporation and conse-

quent concentration of the solvent solution are avoided. The same technic as used for liquids is followed from this point on.

The *schlieren* method of determining the solubility of organic substances was tried on 28 compounds. The results are given in Table IV. These results indicate that the *schlieren* method of determining solubility places each compound in the correct group according to Kamm. The method has the advantages of great simplicity and speed.

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RECEIVED June 8, 1938. This is the second paper in this series. For previous article, see reference (2).

# Microscopical Determination of Potassium with Naphthol Yellow S

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Potassium may be determined qualitatively in the presence of ammonium by means of naphthol yellow S. Ammonium, cesium, lithium, magnesium, and sodium ions do not react with the reagent to form insoluble crystalline salts. Cupric, lead, rubidium, and silver ions form precipitates and may mask the microscopical test for potassium.

RECENTLY Clark and Willets (4) have reported the use of a new reagent, naphthol yellow S (2,4-dinitro-1-naphthol-7-sulfonic acid), for the qualitative macrodetection of potassium. Since the ammonium ion does not interfere with this test, it was decided to investigate the possibilities of using this reagent in the determination of potassium by microscopical methods.

One of the best micromethods for the detection of potassium ion uses chloroplatinic acid (8). However, the ammonium ion (as well as rubidium, cesium, and tellurium) forms with the reagent insoluble crystals which are isomorphous with those of potassium (2). The perchloric acid (5), bismuth sulfate, and tartrate tests (8) also serve for potassium-ion determination, but the salts formed are isomorphous with the insoluble ammonium salts. Thus, in all these tests the ammonium ion must be removed from solution before proceeding with the test for potassium.

### Solutions Used

The naphthol yellow S used for the test reagent was thrice recrystallized from aqueous solution. The original material had previously been utilized for the preparation of 2,4-diamino-1-naphthol-7-sulfonic acid according to the method of Lauterbach (7). The product when further recrystallized from hydrochloric acid yielded the trihydrate mentioned by Knecht and Hibbert (6). The physical constants could not be used to determine the purity, as the literature merely records (6) a melting range of 140–150° C. with decomposition occurring at 175° C. The product used melted between 148° and 149.5° C. Although Clark and Willets (4) reported a greater sensitivity with 2 and 5 per cent solutions, the reagent solution used in this laboratory was more dilute (an aqueous one saturated at 20° C.) because of the difficulties involved in using warm solutions in microtests. When a drop of the test solution (with no further dilution) was placed on a slide it was found that with a room temperature of 23° C. one had to wait 13 to 17 minutes before crystals, discernible under the microscope, formed.

In testing for sensitivity, solutions varying in potassium-ion concentration from 0.05 to 40 mg. per ml. were prepared from recrystallized reagent grade potassium chloride.

In observing the effect of related ions on the reagent and of the presence of foreign ions on the potassium-ion determination, solutions of c. p. sodium chloride, lithium bromide, ammonium chloride, cesium chloride, rubidium chloride, silver nitrate, lead nitrate, magnesium acetate, and cupric nitrate, containing 40 mg. per ml. of the cation were prepared and used.

### Procedure

In determining the sensitivity of the test, one drop of the test solution containing the cation studied was placed on a slide by means of a platinum loop. A similar drop (approximately 0.04 ml.) of the reagent was placed next to the test drop and the two were brought together by means of a sharpened platinum wire probe. For the foreign ion effect one drop of the solution containing the foreign ion was added to the drop containing the potassium ion before addition of the reagent.



### Sensitivity

When the reagent solution is added to a drop of solution containing potassium ion, well-defined acicular and fiberlike crystals form which may be single, although predominantly occurring as bundles (Figure 1). These crystals are charac-



FIGURE 1. POTASSIUM SALT ( $\times 100$ )

teristically different from the fine, individual unclumped fibers appearing upon slow evaporation of a drop of the reagent solution. Although Clark and Willets report that the reagent yields a positive macrotest with a potassium-ion concentration of 0.39 mg. per ml. (the precipitate taking 5 hours to form), it was found that a concentration of 7.5 mg. per ml. was required to yield a positive microscopical test immediately upon addition of the reagent. This eliminates possible error due to crystallization of the free acid from solution. Obviously, although smaller concentrations may be detected, it is inconvenient to await extremely long periods of time in microtesting. Using the capillary pipet method suggested by Benedetti-Pichler and Spikes (1), and a 0.5 per cent reagent solution, and permitting the mixed drop to stand for 3 minutes, the limit of identification was found to be 1.9 micrograms and the limiting proportion of ammonium to potassium, 200 to 1.

### Effect of Foreign Ions

Neither sodium, lithium, ammonium, magnesium, nor cesium ions yielded crystals of any sort upon addition of the reagent. Rubidium, on the other hand, formed sharply defined acicular fiberlike crystals primarily in the form of bundles. Few individual crystals were formed (Figure 2). However, the great similarity in color, size, shape, and form between rubidium and potassium crystals makes it practically impossible to distinguish between the two. The presence of magnesium, ammonium, and the other alkali metal ions, with the exception of rubidium, has no visible effect upon the potassium crystallization. Semimicrotests were also made to determine whether any of these foreign ions had any macro-effect upon the precipitate. Clark and Willets indicate that the presence of sodium causes a darkening of the flocculent yellow potassium precipitate.

Half-milliliter portions of the 20 mg. per ml. potassium-ion solution were placed in a series of 3-ml. centrifuge tubes. To one of these tubes were added 0.5 ml. of distilled water and 1.5 ml. of the reagent solution. Half-milliliter portions of the foreign

ion solutions were added to the other tube before addition of the reagent. The solutions were well stirred with a platinum wire and then permitted to stand for 10 minutes. Precipitation occurred much more rapidly in those solutions containing the added ions. The tubes were placed in a microcentrifuge and spun at 3600 r. p. m. for 5 minutes. Visual comparison showed no difference in volume or color of the precipitates formed.

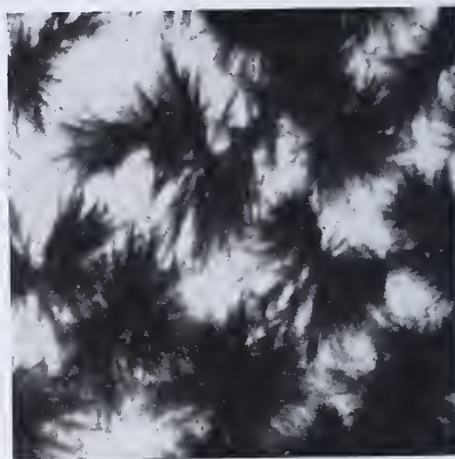


FIGURE 2. RUBIDIUM SALT ( $\times 100$ )

In a further study it was found that silver, lead, and cupric ions also yielded typical crystalline precipitates with naphthol yellow S. These crystals form rapidly. Lead yields smaller, shorter, and thicker fibers as well as small nodules and spherulitic bundles. Cupric copper slowly forms large bundles of needlelike crystals, appearing yellow-green in color under crossed nicols. The potassium is easily distinguishable from the crystals of these three metals.

As is to be expected, a slight concentration of a strong acid prevents the formation of the potassium precipitate. One drop of 6 *N* hydrochloric, nitric, or sulfuric acid is sufficient to prevent precipitation from 1 ml. of the 20 mg. per ml. potassium test solution. However, as much as 1 ml. of concentrated acetic acid has no effect, the precipitate forming as rapidly as from a neutral solution. Work is under way to determine the exact pH range over which the test is valid, as well as the effect of other ions. Because rubidium forms a very insoluble salt with the reagent while cesium does not, it is believed that the reagent may be used to advantage to distinguish between the two. Chamot and Mason (3) say that the differentiation is not easy (between rubidium and cesium), since in most tests dependence must be placed upon differences in solubility alone. It is the author's intention to determine how well this test may be used for such a differentiation.

The foreign anions studied here were chosen because they are the ones most apt to interfere in the determination of potassium.

### Summary

Using an aqueous solution of naphthol yellow S saturated at 20° C. in the microscopical determination of potassium, the limit of concentration has been found to be 7.5 mg. per ml. Permitting 3 minutes for crystallization and using a 0.5 per cent reagent solution, the limit of identification is 1.9 micrograms and the limiting proportion of ammonium to potassium is 200 to 1.

Magnesium, sodium, lithium, ammonium, and cesium ions do not form insoluble compounds with the reagent and



do not affect the test. Rubidium forms crystals similar to those of potassium. This test therefore fails in the presence of rubidium. Although silver, lead, and cupric ions yield crystals characteristically different from those of potassium, these ions may tend to mask its presence.

Small amounts of free strong acids prevent the formation of the insoluble salts, although appreciably large amounts of acetic acid have no effect. Neutralization of the acidic solutions by means of potassium-free sodium hydroxide permits the use of the test.

### Acknowledgment

The author would like to express his appreciation to C. E. Coates for his criticism and suggestions.

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RECEIVED October 20, 1937. Presented before the Microchemical Section at the 95th Meeting of the American Chemical Society, Dallas, Texas, April 18 to 22, 1938.

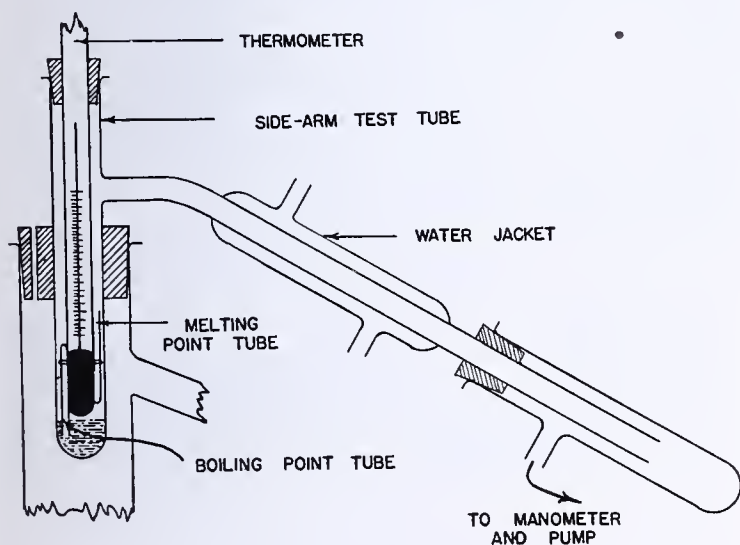
## Melting and Boiling Points on a Micro and Macro Scale under Various Pressures

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A SIMPLE apparatus, shown in the accompanying diagram, has been found very useful for determination of melting, boiling, and freezing points.

The apparatus consists of two side-arm test tubes and a water jacket which need not be sealed on. A Thiele tube is used to avoid the necessity of stirring. The liquid bath is paraffin oil, and the source of heat is gas (microburner), alcohol, or electrical resistance wire, as described by Bergstrom (1). Cleaning is done with alcohol and ether applied with a medicine dropper.



Determinations may be made on either a micro or a macro scale, and the results, without temperature correction, are in close agreement with values given in the literature.

The micro boiling point is determined by a modification of the Shriner and Fuson method (2). Place a drop or two (0.05 to 0.1 ml.) of liquid at the bottom of the tube. Attach a small inverted melting point tube to the thermometer bulb which is

lowered until the open end of the capillary is below the liquid surface. Heat. Remove the flame when a steady stream of bubbles is expelled from the capillary. When the liquid rising in the cooling capillary is level with the outside liquid (vapor pressure equals atmospheric pressure) the boiling point is reached.

The micro boiling and melting points of a solid may be determined in the same operation by placing some crystals at the bottom of the tube and lowering the thermometer into the molten solid after the melting point has been taken.

### Acknowledgment

The author wishes to express his appreciation to Abraham Mazur of The City College of the College of New York for his valuable aid and criticism.

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RECEIVED March 17, 1938.

## Microdetermination of Arsenic

The article on "Microdetermination of Arsenic" [*IND. ENG. CHEM., Anal. Ed.*, 10, 226 (1938)] suggests that the following information might be of assistance to laboratories which have had trouble in the selection of zinc suitable for the analysis. After trying several brands and adding several things to the solution of the acid, this laboratory secured satisfactory results by using "zincum metallicum puriss. chemisch. rein. in bacillis 8 mm., pro anal.," of E. Merck, Darmstadt, Germany.

N. V. LIJM- EN GELATINEFABRIEK "DELFT"

DELFT, HOLLAND



# A New Type of Semimicro Fractionating Column

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A LARGE number of fractionating devices for use on 1 to 10 cc. of liquid have been described in the last decade. Among the simpler and more practicable may be mentioned those of Cooper and Fasce (1), Weston (4), and Craig (2).

In an attempt to devise a column showing high efficiency, large throughput per hour, and low tendency to slugging, a number of columns using rotating members as packing were tested. The form finally adopted has a metal band rotating at about 1000 r. p. m. in place of the usual packing or indentations. The complete apparatus for use at atmospheric pressure on solutions of 1 to 10 cc. is shown in Figure 1.

The length of the condenser was 10 cm. (4 inches), that of the column proper 37.5 cm. (15 inches). The column was a length of Pyrex tubing of 6-mm. inner diameter, to which the heating jacket was sealed. Nichrome wire wrapped around the jacket was used to provide approximately adiabatic conditions in the column. The boiler was placed on an asbestos board provided with a hole slightly smaller than the bulb and heated with a microburner. Asbestos cord was used to provide partial insulation of the portion of the boiler above the asbestos board.

The assembled apparatus was tested with a 2.52 mole per cent solution of carbon tetrachloride in benzene and with a mixture of 1 cc. of methanol and 1 cc. of water.

Table I shows the results obtained with the band rotating at 1000 r. p. m. Using the refractive index-mole per cent

data and curves of Zawidzki (5) and the methods of calculation outlined by Walker, Lewis, and McAdams (3), between 15 and 16 theoretical plates for the 37.5-cm. (15-inch) column and still head combined were obtained. Since the empty column with same still head showed only 4 plates, the still head evidently could not have added more than 2 to 3 plates and the spinning column must have shown at least 13 plates for its 37.5 cm. (15 inches) of length or almost one plate per inch under total reflux. An interesting and somewhat unexpected fact developed was that the column did not reach equilibrium with this mixture in less than 1 hour of total reflux. Equally unexpected was the fact that its tendency to slugging is so low that the 6-mm. inner

diameter column could be operated with a reflux above 2 drops per second, although, as the results show, the efficiency was lowered somewhat by such a high reflux rate.

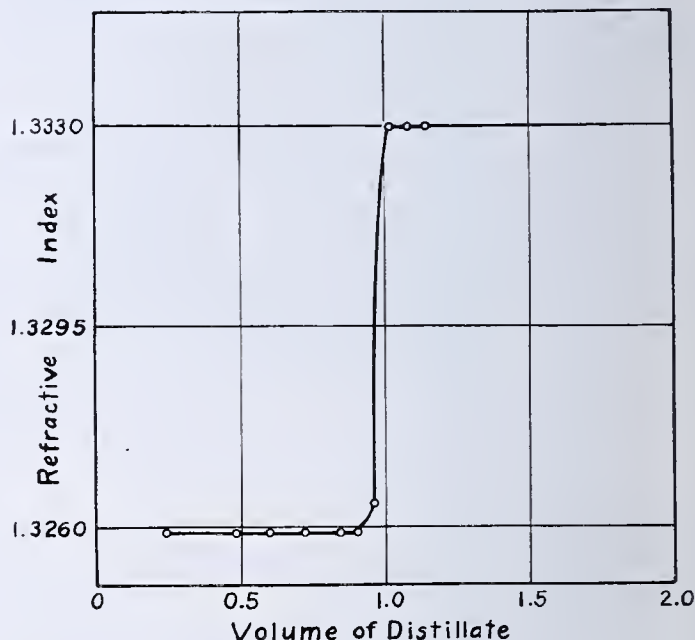


FIGURE 2. DISTILLATION OF 10 CC. OF METHYL ALCOHOL IN 10 CC. OF WATER

Figure 2 shows that the relatively simple methanol-water mixture can be cut in 80 minutes to yield only 1 cut of 0.06 cc. that is not practically pure methanol or water.

TABLE I. TESTS FOR EFFICIENCY  
(100% reflux for 80 minutes)

Reflux Drops/sec.	Rotator R. p. m.	Mole Per Cent $\text{CCl}_4$ In residue	Mole Per Cent $\text{CCl}_4$ In distillate	No. of Theo- retical Plates	H. E. T. P. Inches
1	1000	1.96	26.6	15	1.0
2	1000	2.01	14.2	9.5	1.5
1	0	2.04	4.82	4	3.8

Since the power required to rotate the band is very low, it should be possible to use a very small steel shaft and packing box and operate under vacuum, provided the slow air leak at the stuffing box is not injurious. Such a column is now in use in fractionation of esters of petroleum acids, but no tests of efficiency have been run.

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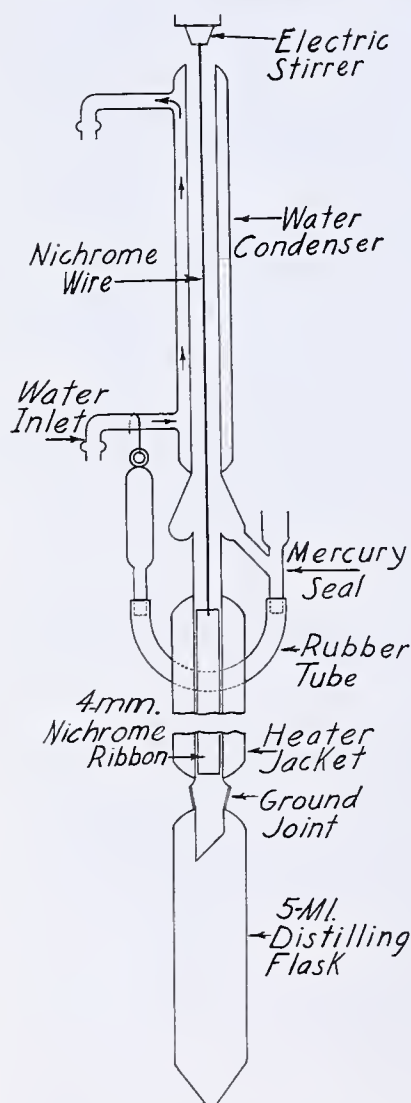


FIGURE 1. APPARATUS



# A New Microphotometer

## For Analyzing X-Ray Diffraction Patterns of Raw Cotton Fiber

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AT NO PERIOD during the history of the cotton industry in America has there been a greater demand than at the present time for information concerning the properties and characteristics of raw cotton fiber and their effects on the spinning qualities. These demands come from cotton breeders, buyers, manufacturers, and consumers and are due in large part to the increased production of foreign cottons and to competition of artificial fibers.

An attempt is being made in the Cotton Utility and Standards Research Section of the Bureau of Agricultural Economics to determine the most reliable measures of cotton quality and to develop more rapid methods for evaluating the known factors. Tensile strength is considered to be one of the more important factors affecting quality in cotton fibers. The strength may be determined by the "Chandler bundle method" (1) or any other method which takes into account the cross-sectional area of the fibers, but reliable methods so far developed are slow and laborious.

The object of this series of studies is to develop a more rapid method for estimating or measuring the tensile strength of raw cotton. The application of x-ray technic to this problem was first undertaken by members of the staff of the Bureau of Agricultural Economics, in informal coöperation with Wayne A. Sisson (3), who was at that time working at the University of Illinois as a senior fellow of the Textile Foundation and a collaborator of the Bureau of Agricultural Economics. These studies showed a relatively high degree of correlation between certain dimensions of the x-ray diffraction patterns and the Chandler strength of raw cottons.

The method used by Sisson to measure the x-ray diffraction patterns was relatively slow and the equipment was subject to a large personal error. A single operator would occasionally obtain a difference of 10 to 15 per cent in measuring the same pattern at different times, and even greater variations were found between different operators. These errors were traced to the microdensitometer, which among other things showed a difference in color in the optical field when changing from the lightest to the darkest part of the x-ray pattern. The operator was therefore required to match intensity of light on two objects which differ in color. It became necessary to obtain a more practical method for measuring the x-ray patterns, and it was apparent that no commercial instrument was suited for this particular problem. The present paper reports the progress of the investigation, including a description of the instrument developed for measuring the tensile strength of raw cotton fibers from the x-ray diffraction patterns.

At least five major demands had to be satisfied. Precision was of first importance because of the small differences in intensity to be measured. Speed of operation was also of primary importance, since it is necessary to measure a large number of patterns in standardizing the method. It was desirable to make the instrument flexible, so that modifications could be made. The instrument must be simple and easily operated by an ordinary laboratory technician. A slight difference in cost could be sacrificed in order to get these characteristics, but the price must not be prohibitive. With these characteristics in mind, the simplest arrangement that gave promise of success was chosen.

### Description of Microphotometer

A microphotometer has been developed which consists essentially of a constant light source, a simple optical system for limiting the illumination to a very small section of the pattern, a means of measuring the light transmitted by this section, and a method of moving the desired portion of the pattern into the optical path.

Figure 1 shows a side view of the microphotometer which was designed by the authors and built in the shops of the Bureau of Agricultural Economics. Except for the instrument panel on the front (Figure 2), which is of aluminum alloy metal, and the top cover of brass plate, the main case is constructed of plywood. The photoelectric cell, *a*, of Figure 1 (Photocell made by the Westinghouse Electric and Manufacturing Company) is located directly below the photo-exciter lamp, *b*, and the light is focused through a slit in the top cover of the box. The film is placed on the mechanical stage, *d*, between the lamp and the photocell, so that it just clears the raised section of the cover in which the slit is located. The film can be rotated or moved back and forth, to bring any portion of the pattern under the light beam. The photoelectric cell is connected to a galvanometer, *g*, of the reflecting type (sensitivity 0.0024 microampere per mm.).

Figure 2 shows the translucent galvanometer scale across the end of the box which is illuminated by a spot of light from lamp *e* (Figure 1). A cross hair is placed in front of the lamp in such a position that its image is formed on the scale.

A 3-candle-power, 6-volt, 0.5-ampere automobile tail-lamp bulb was found to be satisfactory for a photo-exciter lamp. The lamp voltage is controlled by means of two rheostats of 10 and 100 ohms resistance connected in parallel.

The housing for the photo-exciter lamp is constructed of aluminum alloy and has a ventilator in the top to prevent overheating in case a large lamp is necessary. The lens system consists of two plano-convex lenses with diameters of 24.5 mm. each, and focal lengths of 51.2 mm., mounted 2.5 cm. (1 inch) apart with the curved sides facing each other (*C*, Figure 3). The tubular housing, which was made of two sections, one 7.6 cm. (3 inches), the other 2.5 cm. (1 inch) in length, permits a total movement of the lenses of 1.9 cm. (0.75 inch). The shorter section tapers at the lower end so that it has an aperture of 0.48 cm. (0.19 inch). The lamp housing is adjusted so that the small end of the tube comes to rest directly above the slit. The film is placed between the end of the tube and the slit, and an image of the filament of the lamp is focused on the slit.

Figure 4 is a view looking down on the top of the instrument. The photo-exciter lamp is held in position by means of an arm, which fits on a post, *h*. The post is a steel rod about 2.2 cm. (0.875 inch) in diameter, mounted by means of a shoe on the side of the case. The arm connecting the lamp housing to the post is about 5 cm. (2 inches) wide at the narrowest point (Figure 2) and 0.6 cm. (0.25 inch) thick. The arm may be lengthened or shortened slightly by adjusting the nut on a bolt extending through the flanges of a loop, *j*, near its middle (Figure 4). The lamp housing can be raised or lowered on the post, since the sleeve of the arm rests on a clamp which is adjustable on the post. The lower edge of the sleeve adjacent to the clamp fits into a circular groove in the clamp which also contains a V-shaped groove into which the beveled edge of the projecting arm comes to rest. In this way, the lamp can be readily lifted out of position and swung around out of the way while exchanging films, but returns to the same position each time it is placed over the film.

The compound mechanical stage with which the patterns are centered and brought into position for the measurements is made of three units. The large square metal plate (1, Figure 4) is movable in the direction parallel with the long axis of the instrument. It rides on two tracks, one of which contains a groove to keep the stage in a fixed position perpendicular to the direction of movement. This stage moves by means of a rack and pinion and has a metric scale with a vernier reading to 0.1 mm.



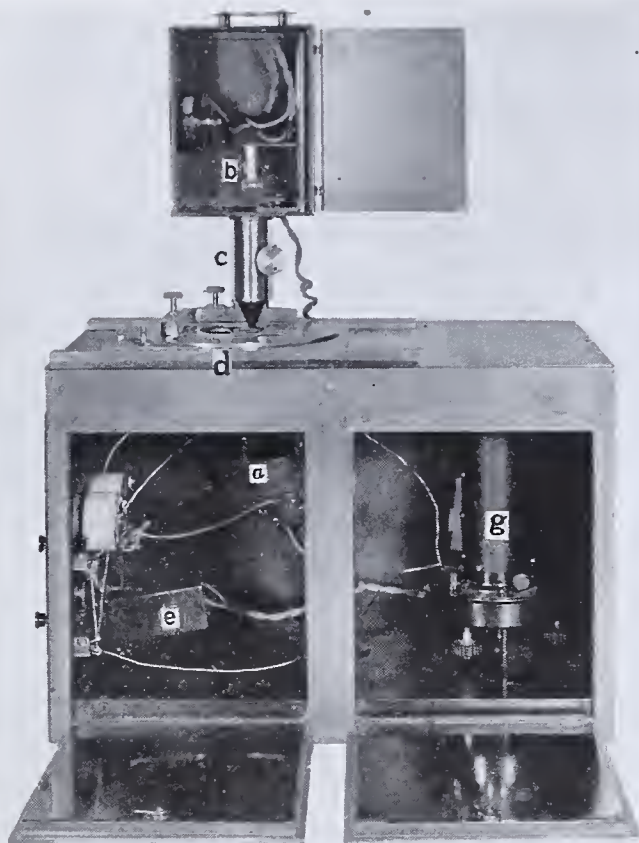


FIGURE 1. SIDE VIEW OF MICROPHOTOMETER  
Showing various parts through opened doors

The second unit (2, Figure 4) consists of a rotary stage built into the large square stage. It is 19 cm. (7.5 inches) in diameter and is calibrated in degrees, with a vernier reading to 0.1 degree. The central portion of this stage is removable, so that a variable-sized central opening can be used, depending on the size of the x-ray pattern to be measured. Ability to match the size of the pattern with the central opening aids considerably in centering the films. The rotary stage is revolved by means of a gear which permits accurate adjustment.

The third unit (3, Figure 4) is similar to a microscope mechanical stage, but is adapted for x-ray films. One carriage of this stage contains two thin metal arms, 0.08 cm. (0.03 inch) thick and 0.6 cm. (0.25 inch) wide which ride flush with the surface of the rotary stage. A steel spring on each arm holds the film in position. Cross lines drawn on an unexposed film are slipped under the metal arms and adjusted over the central opening of the rotary stage to facilitate centering of the pattern. For final adjustment, the cross lines are removed, the exciter lamp is placed in position, and the film is accurately centered with the aid of the galvanometer.

A section of the top cover of the case beneath the mechanical stage, about 5 cm. (2 inches) in diameter at the base and 1.9 cm. (0.75 inch) at the top, is raised in the form of a section of a cone (*n*, Figure 5). The top portion of this cone is covered over except for a circular hole about 2.5 mm. in diameter, about 0.6 cm. (0.25 inch) from the center. This opening is located so that a line drawn through its diameter and the diameter of the raised portion of the cover is parallel with the movement of stage 1 (Figure 4) into which the rotary stage is built. Such a line would bisect the rotary stage and the pinhole cap when they are in position.

Two metal caps, each of which fits over the top of the conelike projection, were constructed. Each cap contains a series of pinholes or openings, one a series of five circular holes, the other a series of four rectangular slits, all located 0.6 cm. (0.25 inch) from the center of the cap, so that any one can be rotated into position. The circular pinholes are 0.5, 0.75, 1.0, 1.5, and 2.0 mm. in diameter, respectively. Three of the rectangular slits are arranged with their long axes in the direction of radii of the cap and the fourth is perpendicular to a radius. The three slits along the radii may be used to determine the intensity around an arc or ring, whereas the other may serve to determine the distance between rings or spots or the relative intensity of the individual rings. The openings along the radii are  $0.5 \times 1.0$ ,

$0.5 \times 1.5$ , and  $0.5 \times 2.0$  mm., respectively, and the one perpendicular to the radius is  $0.5 \times 1.0$  mm. The smallest of the radial rectangular slits has been found most satisfactory.

For the particular purpose for which this instrument was designed, readings need not be made in standard units, since the technic depends solely upon ratios of a given set of measurements. However, means were provided for calibrating the apparatus so that, if desired, the readings can be expressed in the usual terms of density, transmission, or opacity. This is done by means of a set of three "neutral" glass filters with densities of 0.357, 0.603, and 1.19, respectively. The first was mounted permanently in the instrument, so that it can be swung into position above the photocell at any time.

The luminous transmissions of the filters for the conditions of operation have been calculated and the results may be used to convert the galvanometer readings to actual transmissions when so desired. (The spectral transmissions of the filters were measured with a General Electric recording spectrophotometer by the Bureau of Standards, U. S. Department of Commerce. Data on the spectral response of the Photocell were also supplied by the Bureau of Standards.) The filters are sufficiently "neutral" so that small errors in color temperature of the lamp or in color response on the cell will not appreciably affect the values obtained for their luminous transmission.

Although exact linearity of response of the photocell to light intensity is not essential to this particular problem, such a response was found to exist over the entire range of the light intensity used. By using low light intensity, with a sensitive galvanometer, the galvanometer deflections were found to be proportional, within the limits of accuracy in

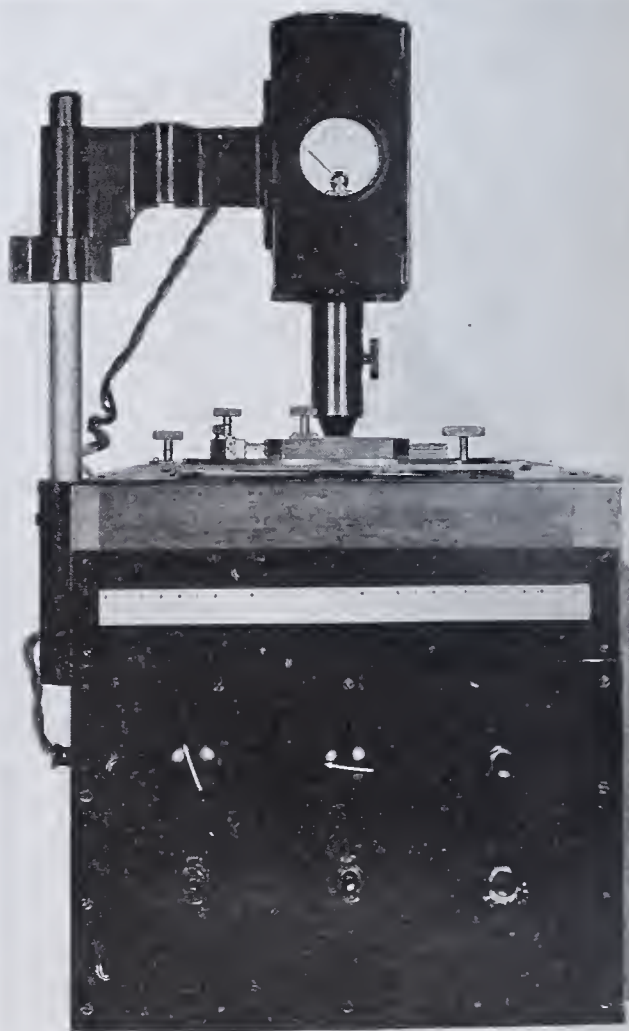


FIGURE 2. FRONT VIEW OF MICROPHOTOMETER



reading the scale, to the transmissions (0.440, 0.250, and 0.0646, respectively) of the filters.

The microphotometer has been found very stable and reliable. The 6-volt lamp used as a source of illumination on the film is operated at about 4.7 volts from a heavy-duty battery and has remained stable over long periods of time. When properly adjusted, the galvanometer readings, as checked by the filter, did not drift more than 1 mm. in an hour and often not enough in this time to be noticeable on the scale. Changes over long periods of time in the lamp or in the photocell will not affect the results. The only exception is the error which would be introduced if the shape of the response curve of the photocell should change. In over a year's use, such change as may have occurred was not sufficient to be observed in repeated measurements of the standard filters.

### Method

The bundles of fiber were prepared in the same way as in the Chandler method (1) except for wrapping. After combing and adjusting to the correct size (0.3-cm., 0.125-inch, circumference) they were placed in the clamps and wrapped from one end to the opposite end, using a single thread with a 907-gram (2-pound) weight on it. Cellulose acetate or collodion was then placed on the wrapped thread and allowed to dry. A portion of the thread near the middle of the bundle was then cut away, exposing the parallel fibers—the collodion preventing the balance of the thread from coming off.

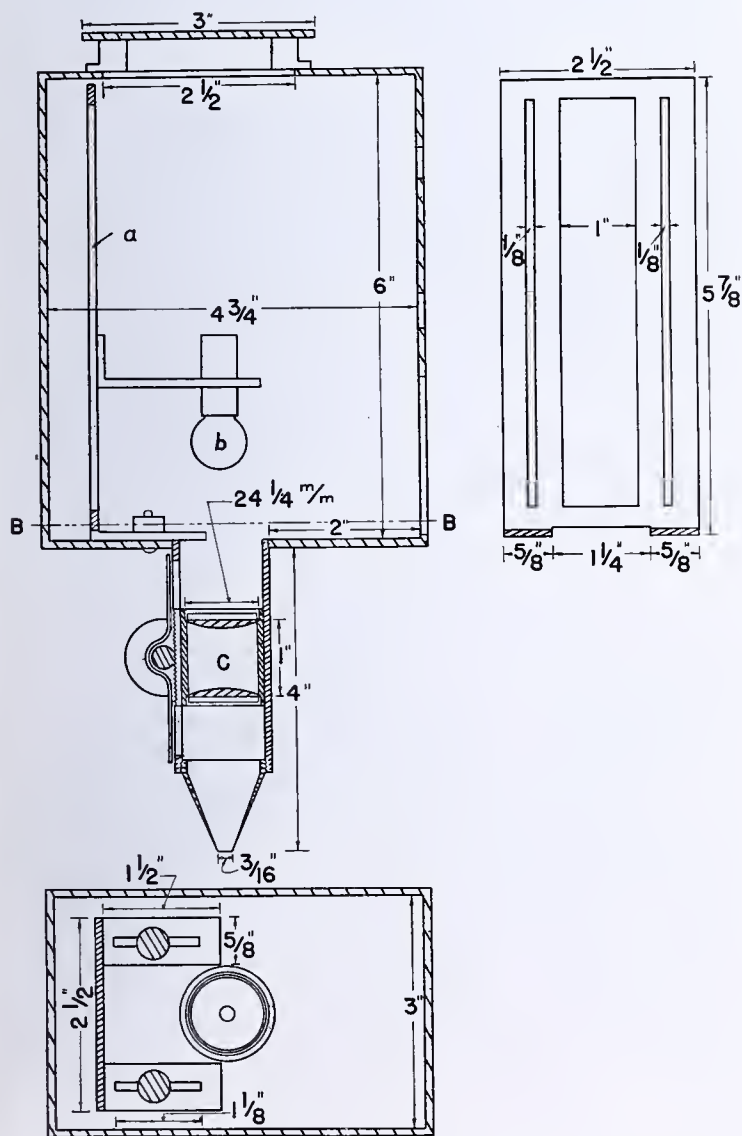


FIGURE 3. CROSS SECTION OF PHOTO-EXCITER LAMP HOUSING  
b. Lamp C. Lens system

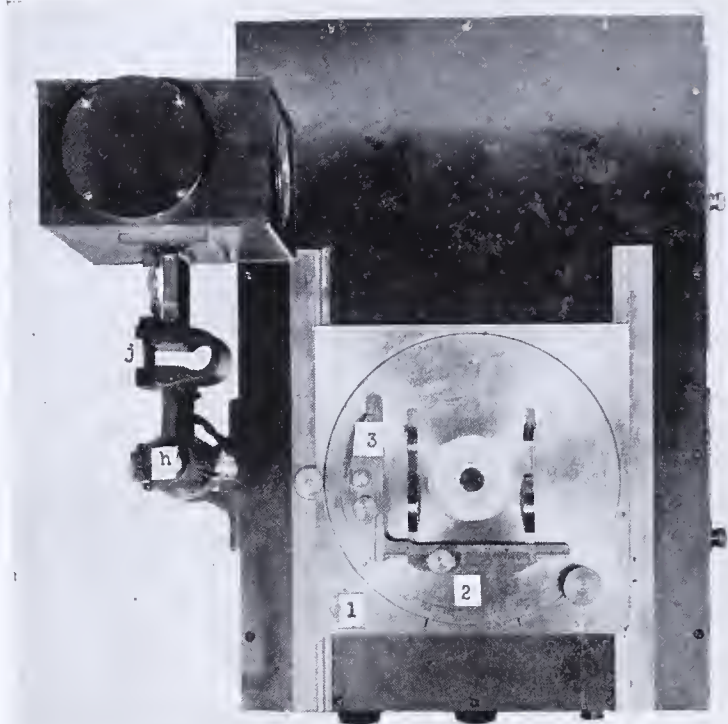


FIGURE 4. TOP VIEW OF INSTRUMENT  
Showing compound mechanical stage

The x-ray diffraction patterns were obtained by passing a parallel beam of copper radiation through this bundle of paralleled cotton fibers held with the long axis perpendicular to the x-ray beam. The diffracted radiation was allowed to fall upon a flat photographic film placed 4 cm. from the center of the bundle. Because of their prominence and simple relation to the fiber axis, the arcs resulting from the 002 plane (Figure 6) were measured.

The method consists essentially in determining relative lengths, in degrees, of these arcs. Since the arcs taper off gradually, it is difficult to set an end point for practical use in determining their lengths. Sisson and Clark (4) tried several measures, including the angular distance from the point of maximum density to the points of the median, the mean, and the standard deviation of density.

In the present set of measurements, various criteria have been tried, based on transmission, opacity, and density. As a measure of orientation, the angular displacement from the point of maximum blackening to the point where 60 per cent of maximum transmission occurs is being used. This is equivalent to 40 per cent of the maximum absorption and, because of a slightly greater convenience in calculating, the scale of the microphotometer has been placed so as to show the absorption of the film. An important advantage over the method based on density is that a better relation is obtained with shorter exposures. Best results are obtained when the maximum density is about 0.5, whereas it is indicated that the maximum density should be around 1.0 if the measurements are based on density. This represents a saving of at least 50 per cent in exposure time—an important factor in a process of this type.

The details of measurement are as follows:

The film is centered accurately upon the stage, so that the arcs from the 002 plane will remain over the pinhole while the stage is being rotated through 360°. This is readily done by centering the film with the aid of the removable cross lines and then checking the centering by galvanometer readings at a few points around the circle. The positions on the stage corresponding to maximum blackening are then recorded. The galvanometer readings are



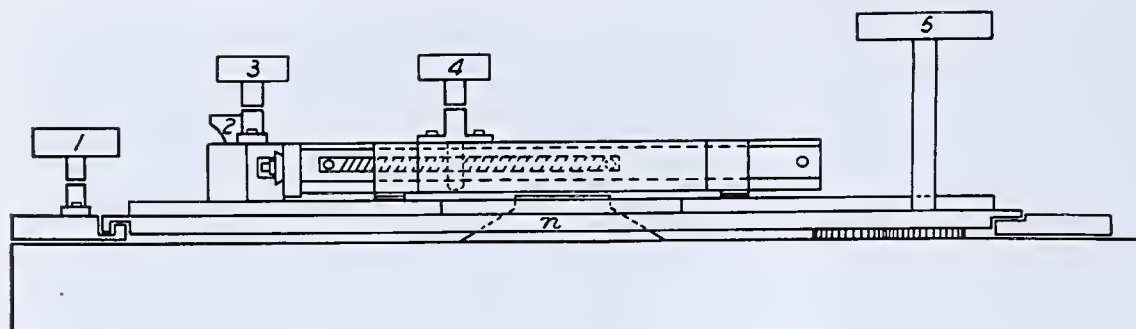


FIGURE 5. DIAGRAM OF MECHANICAL STAGE

Showing details of construction in relation to raised portion,  $n$ , of base plate

taken at a point of maximum blackening and at  $90^\circ$  from this at a point of minimum blackening. Forty per cent of the difference between these two readings is then added to the minimum reading, and the stage is rotated between these two positions until the point is found at which the galvanometer shows the calculated reading. The difference between the reading on the scale of the circular stage at this point and at the position of maximum blackening is the angular distance of the point of 40 per cent absorption (60 per cent transmission). This measurement is made in each of the four quadrants of the circle and the average value is used.

This instrument as used is not adapted for measuring absolute density or transmission with a high degree of accuracy. Furthermore, the "absorption" values contain a reflection factor which has not been taken into account; but for this particular purpose variations in the photographic method far outweigh any possible sources of error in the microphotometer. The difficulties in the photographic method, such as variation in developer strength or in film emulsions, have been studied at some length and further experiments along this line are planned. To date, however, the results show a sufficiently high reproducibility to justify the use of the method under well-controlled conditions.

## Results

The new microphotometer has a number of advantages over such previous instruments as the microdensitometer used by Sisson and Clark (4) and Sisson (2, 3) for analyzing the x-ray diffraction patterns of raw cotton fibers. The compound mechanical stage allows for a more rapid adjustment and the high sensitivity to changes in the blackening of the film assures accurate centering of the pattern. A given operator can accurately measure from two to four times as many

patterns in a day on the microphotometer as on the microdensitometer.

The error of measuring a film on the microphotometer is negligible in comparison with the errors in preparation of sample and the reproducibility of the photographic method. A standard error of  $0.05^\circ$  in the angle of 40 per cent absorption was obtained with the microphotometer when three different operators measured the same patterns repeatedly, whereas a standard error of  $0.52^\circ$  was obtained on the microdensitometer when only two different operators made repeated measurements on the same patterns. This indicates that in addition to being more rapid the microphotometer has a precision approximately ten times that of the microdensitometer.

The Chandler strength values for 30 different cottons were found to be related to the 40 per cent angle, as obtained from the x-ray diffraction patterns, by the equation  $S = 193.5 - 3.18A$ , where  $S$  represents the strength and  $A$  the angle. The calculated and observed Chandler strengths may be compared by referring to columns two and three of Table I. The regression line and the coefficient of correlation of the observed strengths and the angle are given in Figure 7.

The angle, as obtained, may be considered as an indication of the common orientation of the long axis of the cellulose chains in relation to the long axis of the fiber. This angle can be representative of the orientation only when the photographic conditions are kept constant. In measuring different patterns of the same bundle, where maximum density varied from about 0.5 to 1.0, the angle, as obtained from the absorption, changed as much as  $5.5^\circ$  to  $6^\circ$ . When good clear films are used with a known strength of developer, the data may be corrected to a given absorption or density and a better correlation obtained. If the films show signs of

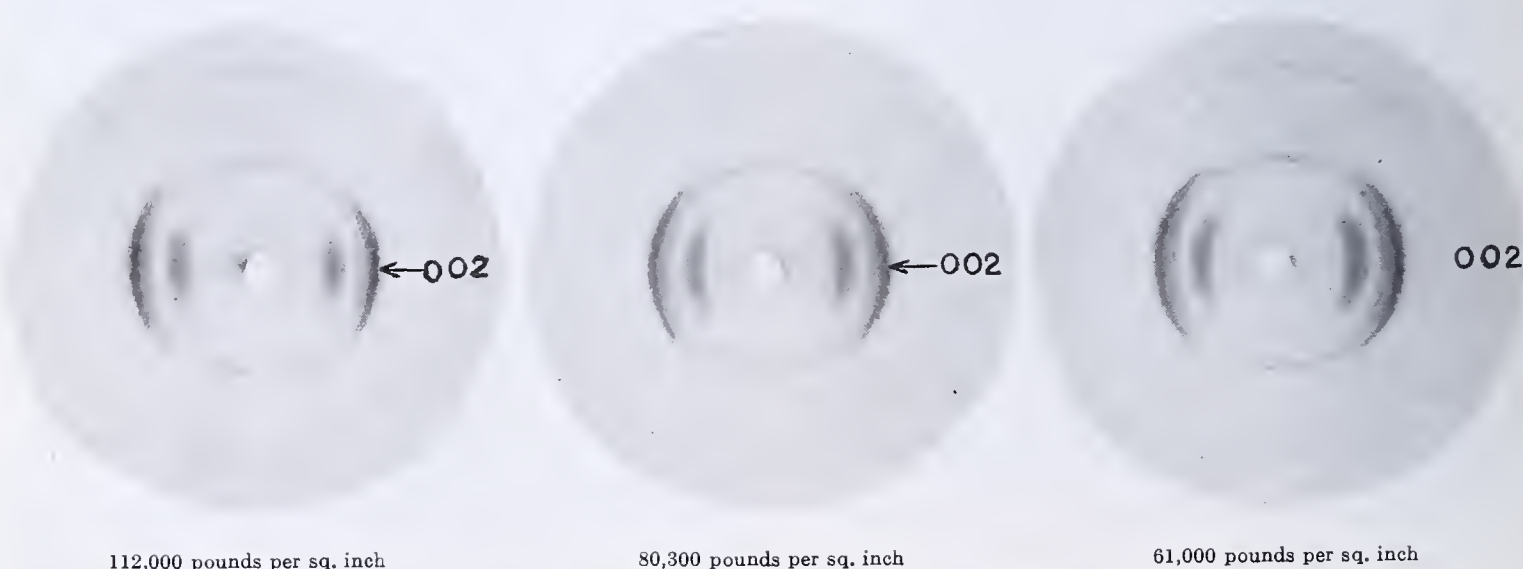


FIGURE 6. TYPICAL X-RAY DIFFRACTION PATTERNS FOR BUNDLES OF COTTON FIBERS OF DIFFERENT CHANDLER STRENGTHS



TABLE I. THE 40 PER CENT ANGLE AND THE CALCULATED AND OBSERVED CHANDLER STRENGTHS OF 30 SAMPLES OF COTTON

40% Angle Degrees	Calculated Chandler Strengths 1000 lb./sq. inch	Observed Chandler Strengths 1000 lb./sq. inch
43.6	54.9	60.0
43.4	55.5	62.6
38.2	72.0	65.2
38.5	71.1	67.2
36.5	77.4	71.5
38.1	72.3	73.4
36.0	79.0	75.3
34.0	85.4	77.9
33.6	86.7	80.0
34.9	82.5	83.2
33.5	87.0	85.8
33.7	86.3	88.6
32.6	89.8	90.0
31.4	93.7	90.2
31.0	94.9	91.8
31.8	92.4	92.0
32.7	89.5	93.0
30.7	95.9	93.1
31.5	93.3	95.5
29.6	99.4	97.9
29.3	100.3	98.5
28.6	102.6	101.0
32.3	90.8	101.0
30.1	97.8	102.2
29.4	100.0	102.2
29.7	99.1	102.6
29.1	101.0	103.2
29.5	99.7	104.0
28.4	103.2	105.0
27.6	105.7	105.2

deterioration or the developer varies too widely in strength, the changes in the angle do not have a simple relationship to the blackening and no known correction can be successfully applied. The method based on the absorption (or transmission) was found to be affected less by variations in the photographic details than was that based on either the density or opacity.

The estimated Chandler strengths agree fairly well with the observed values (compare columns two and three of Table I). Each calculated value is based on one bundle of cotton from a given sample, whereas the observed Chandler strengths are the averages of ten bundles from each sample. A slightly lower coefficient of correlation was obtained when the angle was calculated from the opacity, the density, or the equivalent exposure time.

The data in Table I and Figure 7 were obtained from patterns of bundles of raw cotton photographed while the bundles were under a tension of 6.8 kg. (15 pounds). The purpose of the tension was to remove the natural wave or curl of unstretched cotton fibers and thus secure a better alignment of the fiber axes. Tension may be applied by any convenient method that gives consistent results.

When bundles from 48 samples representing different cottons were photographed without tension on the bundles, a correlation coefficient of  $-0.82$  between Chandler strength and the 40 per cent angle was obtained, as compared with  $-0.95$  when 30 samples were photographed with tension. However, the patterns for the "no tension" series were obtained under a wide range of photographic conditions. When these conditions are not kept relatively constant, the correlation coefficient would not be expected to be as high, even after the results are adjusted to a common absorption value. Correlation coefficients as high as  $-0.88$  have been obtained for small numbers of bundles photographed without tension. Further work is planned to determine whether tension is essential and, if so, the amount necessary.

Summary and Conclusions

A microphotometer for measuring x-ray diffraction patterns has been developed and successfully used to measure

patterns of raw cotton fibers. It consists of a constant light source focused on the pattern, a measuring device composed of a photoelectric cell and galvanometer system, and a compound mechanical stage for holding and moving the patterns under the light beam while measuring them. The instrument is stable and shows a high degree of precision in repeated measurement of the same x-ray diffraction patterns of raw cotton fibers. A coefficient of correlation of 0.95 between single x-ray patterns from each of 30 different cottons and their Chandler strength was obtained when the samples were photographed under tension. Lower correlations were obtained when no tension was used. These results indicate that the x-ray method may be used with considerable precision to estimate the strengths of undegraded raw cotton.

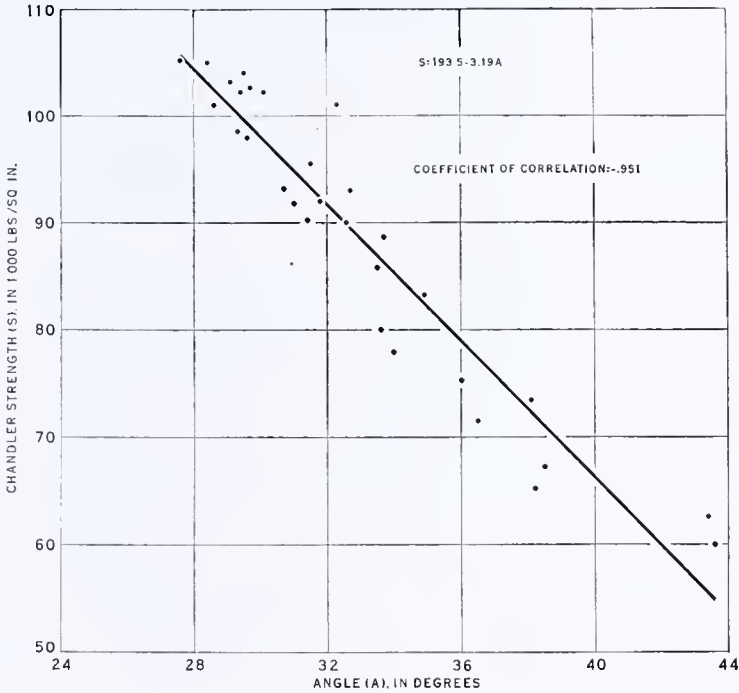


FIGURE 7. RELATION OF CHANDLER STRENGTH TO THE 40 PER CENT ANGLE AS MEASURED ON X-RAY DIFFRACTION PATTERNS

Further experiments are planned to determine the effects of preparation of sample, tension, fiber-wall development, and biological decay on the x-ray patterns and their relation to the tensile strength of raw cotton.

Acknowledgments

The authors wish to express their gratitude to C. M. Conrad, senior cotton technologist, U. S. Department of Agriculture, for numerous helpful suggestions and criticisms on the experimental work and preparation of this manuscript; and to J. F. Barghausen, who coöperated with the authors and offered many helpful suggestions regarding the construction of the instrument.

The authors are indebted to the Tung-Sol Lamp Works, Inc., for the temperatures of the lamp at different voltages.

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# A Constant-Temperature Bath for Stodola's Acetylation Microapparatus

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STODOLA'S method (1) for the microdetermination of hydroxyl and amino groups involves quantitative acetylation of these groups, which is carried out in a small flask

intermittent attention on the part of the operator to maintain this temperature.

The apparatus described maintains the required temperature indefinitely without attention. This frees the operator, and the use of two reaction flasks allows him, while one reaction is in progress, to titrate the previous reaction, clean the flask, and weigh out the sample for the next reaction without interruption. Over the course of four consecutive analyses as much as 2 hours may thus be saved. The apparatus employs the principle of the Abderhalden dryer, in that the desired temperature is maintained by the vapors of a suitable refluxing liquid (water). The reaction flask of Stodola's apparatus is partially immersed in glycerol in a well which is heated by the vapors from the boiling liquid in the large flask, A. The vapors are returned by a short water condenser which is connected in series with, and following, the condenser of Stodola's apparatus.

Glycerol is used in the well because it is very easily washed from the reaction flask before the titration is carried out. Mineral oil is inconvenient here, because it is hard to wipe it from the reaction flask. Mercury could be used if the laboratory were well ventilated, but it is not recommended on account of possible danger to the operator.

Flask A is conveniently fashioned from a 50-cc. Pyrex Erlenmeyer. The dimensions as shown in the figure are adjusted to suit the measurements of the acetylation flask.

To use the apparatus a small amount of water is placed in flask A and the condenser water is turned on. The well is filled about two-thirds full of glycerol to assure good thermal contact with the reaction flask, and the water is brought to a boil with a microburner. The apparatus needs no further attention. A little zinc dust in flask A will promote smooth boiling.

This type of bath is, of course, suitable for other reactions which require a constant temperature over a period of time.

## Acknowledgments

The author wishes to acknowledge with thanks the aid given by James Cason and Walton Geiger in developing and testing this device.

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RECEIVED May 3, 1938

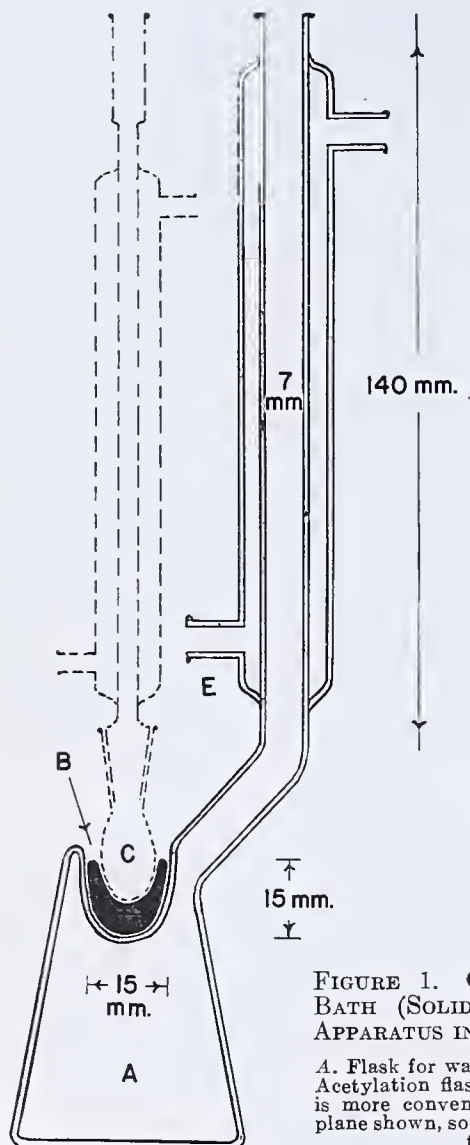
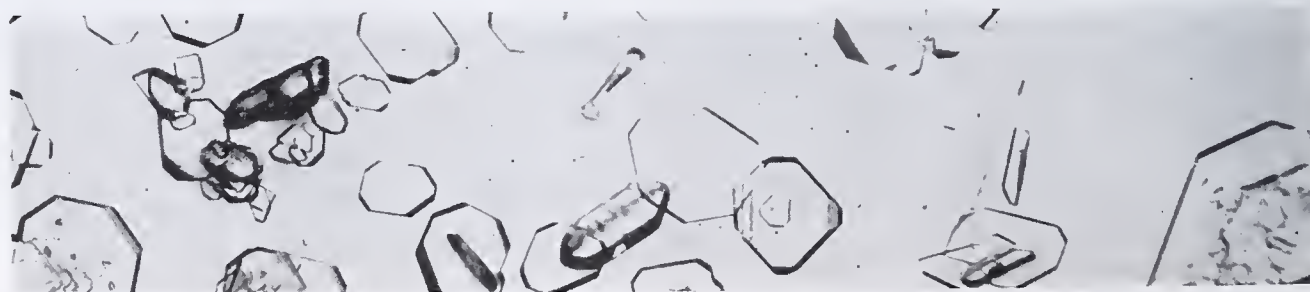


FIGURE 1. CONSTANT-TEMPERATURE BATH (SOLID LINES). ACETYLATION APPARATUS IN PLACE (BROKEN LINES)

A. Flask for water. B. Glycerol in well. C. Acetylation flask. Condenser jacket tube E is more conveniently placed at 90° to the plane shown, so as to be out of way of acetylation apparatus

fitted with a vertical condenser (shown with broken lines in the diagram). For complete reaction the contents of the flask must be held at 95° to 100° C. for one hour. This is ordinarily achieved by means of a glycerol bath and it requires



BARIUM CHLORIDE (PHOTOMICROGRAPH)

Courtesy, M. L. Willard



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Chemical Analysis by X-Ray Diffraction

### Classification and Use of X-Ray Diffraction Patterns

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INDUSTRIAL AND ENGINEERING CHEMISTRY considers itself fortunate in being able to present herewith a complete, new, workable system of analysis, for it is not often that this is possible in a single issue of any journal. Several qualified reviewers assure us that the authors present here a method that is not only workable but so clearly described that their scheme of chemical analysis will be readily understood by all those familiar with x-ray diffraction. The reader does not need to be skilled in crystal analysis; he needs only to be familiar with the bare principles of diffraction.

There is reason to believe that this publication, which is made possible in this form by the generous financial assistance of the Dow Chemical Company, will serve to bring this method of analysis into general use in industrial and consulting analytical laboratories.

THIS paper supplies tabulated data on the diffraction patterns of 1000 chemical substances and gives a scheme of classification which makes possible a routine and valuable use in the chemical laboratory of the Hull method of x-ray analysis.

In 1919, Hull (9) described a new method of chemical analysis by means of x-ray diffraction. He gave the experimental procedure and pointed out the various interesting and important features of the method, emphasizing the experimental simplicity of obtaining the diffraction pattern of a substance and the fact that it requires only a minute amount of material. He gave illustrations of the important fact that the diffraction method tells the state of chemical combination of the elements present in the unknown, and stated the basis for the method: "That every crystalline substance gives a pattern; that the same substance always gives the same pattern; and that in a mixture of substances, each produces its pattern independently of the other, so that the photograph obtained with a mixture is the superimposed sum of photographs that would be obtained by exposing each of the components separately for the same length of time. This law applies quantitatively to the intensities of the lines [provided absorption is negligible for each of the components], as

well as to their positions, so that the method is capable of development as a quantitative analysis."

These unique features would appear to entitle the method to a place of real usefulness in chemical analysis. However, as yet no extensive use has been made of x-ray diffraction in this way. Probably one of the most important circumstances, which at present handicap the general use of the method, is that an adequate file of standard patterns is not available for reference. The method being empirical, standards are necessary. A certain limited amount of work could be done by determining crystal structure, but this is not a practical procedure. For any one person, the assembling of a large library of patterns would be a great task, since it would run into many thousands; also, it is not assured without test that it would be feasible to classify and make use of such a file were it available.

At The Dow Chemical Company it has been found that another useful fact concerning diffraction patterns may be added to those already given by Hull—namely, that the thousands of patterns representing the thousands of different chemical substances can be classified in such a way that they may be easily used for the identification of an unknown, even when the unknown is a mixture of substances.

The basis for this interesting conclusion and the scheme of classification were described in an earlier publication (8). Since that time, there have been many requests to make the data available for general use. The Dow Chemical Company has been very willing to do this, but has postponed publication until this time in order to determine a satisfactory form in which to put the data. When the original negatives are on file, the simplest procedure, after locating the standard by means of the classification system, is to compare negatives directly as to position and intensity of the lines. However, for publication, it is not feasible to make a true reproduction of the negatives. Microphotometer traces would give the data accurately, but would involve a more time-consuming technic than is desirable for routine and economical analysis.

The data of the pattern should be recorded as simply as possible and yet sufficiently accurately for analysis. During the past year such a means has been fully demonstrated and it is now possible to present the diffraction data in a form which may be used by a person in another laboratory. If it appears sufficiently interesting, data on more substances could be made available from this laboratory and perhaps from



many others. The use of the x-ray method of analysis would be greatly extended if crystal structure workers, after they have taken care to get a pure material, would publish the powder data of the material in the same or in an equivalent form.

to use more than the two strongest lines in order to index the patterns.

In the whole index book, there are only 27 subgroups which contain more than 3 patterns and only one which contains more than 5 patterns. The fact that two patterns fall in the same subgroup does not mean that they are identical with respect to

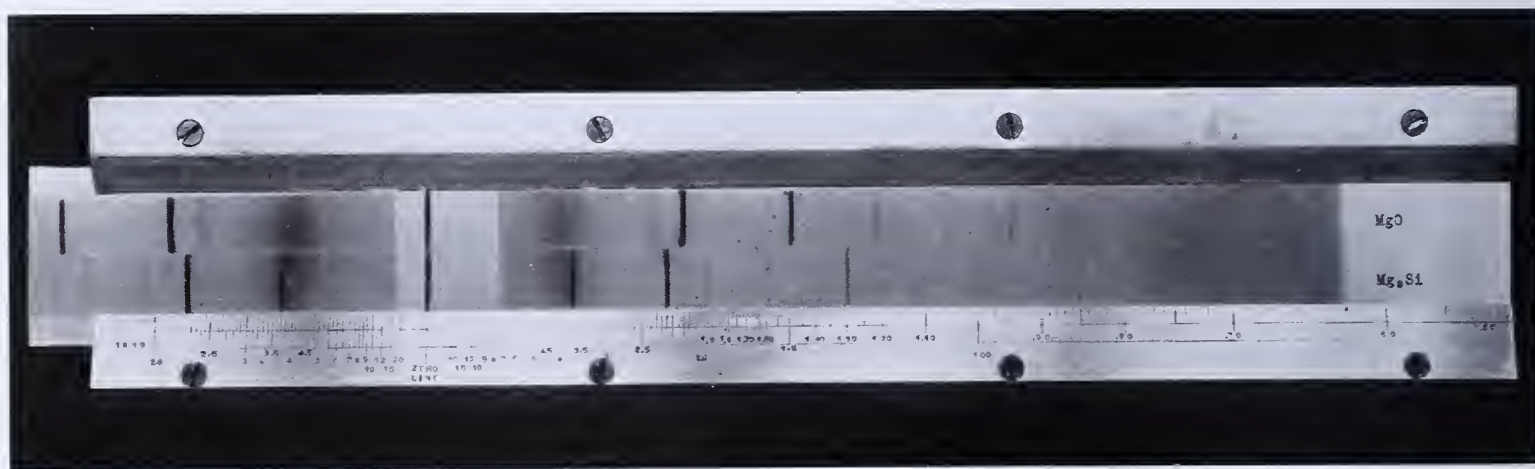


FIGURE 1. ANGSTROM SCALE WITH SYMMETRIC FILM

For those who are already equipped with x-ray diffraction apparatus, the only step necessary to use the data here presented is to compile the index book as described. For those who are not familiar with the details of what is involved in x-ray diffraction analysis, a survey view is given of the apparatus required, the technic of obtaining the patterns, and the method of interpreting the patterns, as well as some illustrations of the field of application of the general method. The present article is based on experience gained in carrying out several thousand actual analyses during the past five years.

### The Classification System

The diffraction pattern, as commonly obtained, consists of a sequence of lines in certain definite positions (on an Å. scale giving the spacing of the crystal planes represented) and of certain relative intensities (Figure 1). The method of measuring the negatives is discussed below, but for the purpose of describing the classification system it can be assumed for the moment that the data have been obtained in the form given in the tables of patterns. The lines lie between 20 Å. and 0.5 Å., and for indexing purposes are grouped into 77 suitably chosen divisions. The sizes of these divisions are based upon experience and are determined by the consideration that they should be larger than the accuracy of measurement of the position of the lines, and should be no more numerous than is necessary to handle conveniently all the patterns without conflict. Actually the size of a division is 5 to 10 times the error of measurement.

From the data of the patterns, the positions of the three strongest lines are read off in the order of decreasing intensity. If two lines have the same intensity value, the rule is to list the one with the greater Å. spacing first. One thus has as a characteristic of each pattern, three numbers in a certain sequence. The patterns are then listed, at the proper place, in an indexed book which is divided and subdivided into the chosen regions. The first number determines the group, the second number the subgroup, and the third number the location within the subgroup. The index book thus consists of 77 sections or groups, each of which in turn contains 77 subgroups. For illustration, three sections of the index book are shown (Figures 2, 3, 4). The index book as it is actually being used provides 15 spaces in each subgroup, but in the illustration these spaces have been omitted. These sections are typical of the average section of the index book and show that among the 1000 patterns listed, it is hardly necessary

their first two lines, since their positions within the divisions may be different and their relative intensities probably will be different. Considering now the coincidences of third lines within a subgroup, there are 11 subgroups in which 2 patterns have the same positions of the third line (with twice the  $\pm$  error of measurement) and 4 subgroups in which 3 patterns have the same third line. In seven of these cases, a measurement of the fourth line serves to distinguish the patterns. (A column is included in the book for recording the fourth line.) However, in practice, after a pattern has been located in the index book (which gives its name and number in the file), the pattern data are referred to in the file and compared directly in all their details. When this is done, for the conflicts still remaining there are only three cases left in which the patterns are not immediately distinguishable from each other. In these cases, if there were nothing easier to do, a more accurate determination of planar spacings by a different x-ray technic would be sufficient. Probably, however, some other information would be available to assist in separating these very occasional conflicts.

Taking into account the number of subgroups and the distribution of the lines as they occur in the type of pattern studied, it is estimated that the index book in its present form, making use of three lines as described, would handle many thousands of patterns. If, for instance, there were 20,000 patterns in the file, there would be a total of only several hundred cases in which one would have to compare his unknown with two patterns from the file, and not more than about twenty cases in which one would have to compare with more than three patterns.

As practiced at The Dow Chemical Company, a second and independent method of listing the patterns is included in the index book. Each of the 77 major groups of the book is followed by a section called the Supplementary Group Index in which (1) all the patterns whose strongest line falls in the major group have their three strongest lines listed in the order 1, 2, 3; (2) all the patterns whose second strongest line falls in the major group have their three strongest lines listed in the order 2, 1, 3; and (3) all the patterns whose third strongest line falls in the major group have their three strongest lines listed in the order 3, 1, 2. An illustration of the use of the Supplementary Group Index will be found among the examples given below.

### Procedure with Unknowns

Suppose that the pattern of an unknown has been obtained and the positions and relative intensities of the lines



FIGURE 2  
Group 2.55-2.50

No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line
	20.00-15.00				4.50-4.40				2.75-2.70				1.75-1.70		
	15.00-12.00				4.40-4.30				2.70-2.65				1.70-1.65		
	12.00-10.00				4.30-4.20				2.65-2.60				1.65-1.60		
	10.00- 9.00				4.20-4.10				2.60-2.55				1.60-1.55		
	9.00- 8.50				4.10-4.00				2.55-2.50				1.55-1.50		
												743	SiC (Cubic)	1.31	
	8.50- 8.00				4.00-3.90				2.50-2.45				1.50-1.45		
	8.00- 7.50				3.90-3.80				2.45-2.40			426	Fe <sub>3</sub> O <sub>4</sub>	1.62	
												979	ZnFe <sub>2</sub> O <sub>4</sub>	2.97	
	7.50- 7.00				3.80-3.70				2.40-2.35			527	MgFe <sub>2</sub> O <sub>4</sub>	2.95	
	7.00- 6.50				3.70-3.60				2.35-2.30				1.45-1.40		
								372	CuO	1.86					
	6.50- 6.00				3.60-3.50								1.40-1.35		
									2.30-2.25						
	6.00- 5.75				3.50-3.40								1.35-1.30		
									2.25-2.20						
	5.75- 5.50				3.40-3.30								1.30-1.25		
									2.20-2.15						
	5.50- 5.25				3.30-3.20								1.25-1.20		
									2.15-2.10						
	5.25- 5.00				3.20-3.10								1.20-1.15		
108	Ba(NO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	3.48		897	SrO <sub>2</sub>	2.00			2.10-2.05				1.15-1.10		
	5.00- 4.90				3.10-3.00				2.05-2.00				1.10-1.05		
	4.90- 4.80				3.00-2.95				2.00-1.95				1.05-1.00		
	4.80- 4.70				2.95-2.90				1.95-1.90				1.00- .90		
855	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O	1.85													
					2.90-2.85				1.90-1.85				.90- .80		
	4.70- 4.60														
					2.85-2.80				1.85-1.80				.80-		
	4.60- 4.50														
					2.80-2.75				1.80-1.75						

SUPPLEMENTARY GROUP INDEX 2.55-2.50

No.	Compound	1st line	2nd line	3rd line	No.	Compound	2nd line	1st line	3rd line	No.	Compound	3rd line	1st line	2nd line
108	Ba(NO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.52	5.1	3.48	127	BeSO <sub>4</sub> ·4H <sub>2</sub> O	2.52	3.90	3.20	362	Cu <sub>2</sub> Fe(CN) <sub>6</sub> ·7H <sub>2</sub> O	2.50	5.0	3.55
855	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O	2.51	4.75	1.85	113	Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	2.51	3.58	4.45	848	Na <sub>2</sub> PbO <sub>3</sub> ·3H <sub>2</sub> O	2.53	4.80	4.62
897	SrO <sub>2</sub>	2.52	3.14	2.00	679	KI	2.50	3.53	4.08	95	BaCl <sub>2</sub> ·2H <sub>2</sub> O	2.54	4.48	2.91
372	CuO	2.51	2.31	1.86	683	KNO <sub>2</sub>	2.50	3.31	2.20	165	CdWO <sub>4</sub>	2.53	3.80	3.05
743	SiC	2.51	1.54	1.31	74	SbI <sub>3</sub>	2.54	3.30	2.14	589	Hg(CN) <sub>2</sub>	2.51	3.72	4.85
979	ZnFe <sub>2</sub> O <sub>4</sub>	2.53	1.48	2.97	999	ZrSiO <sub>4</sub>	2.51	3.29	1.71	164	(CdSO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O	2.51	3.55	4.90
426	Fe <sub>3</sub> O <sub>4</sub>	2.53	1.48	1.61	918	Th	2.53	2.92	1.79	87	Ba	2.51	3.54	2.04
527	MgFe <sub>2</sub> O <sub>4</sub>	2.51	1.48	2.95	749	Ag <sub>3</sub> AsO <sub>4</sub>	2.50	2.74	1.63	349	2CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	2.51	3.51	5.1
					423	Fe <sub>2</sub> O <sub>3</sub>	2.51	2.69	1.84	115	Ba(H <sub>2</sub> PO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.54	3.34	7.8
										84	As <sub>2</sub> O <sub>3</sub>	2.53	3.18	6.3
										726	K <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	2.51	3.09	3.92
										724	KCNS	2.51	2.97	2.79



FIGURE 3  
Group 2.70-2.65

No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line
	20.00-15.00				4.40-4.30				2.70-2.65				1.85-1.80		
	15.00-12.00				4.30-4.20				2.65-2.60				1.80-1.75		
	12.00-10.00				4.20-4.10				2.60-2.55				1.75-1.70		
	10.00- 9.00				4.10-4.00				2.55-2.50				1.70-1.65		
								423	Fe <sub>2</sub> O <sub>3</sub>	1.84			1.65-1.60		
	9.00- 8.50				4.00-3.90				2.50-2.45						
								765	Ag <sub>3</sub> PO <sub>4</sub>	1.66			1.60-1.55		
	8.50- 8.00				3.90-3.80				2.45-2.40						
	8.00- 7.50				3.80-3.70				2.40-2.35				1.55-1.50		
	7.50- 7.00				3.70-3.60				2.35-2.30				1.50-1.45		
	7.00- 6.50				3.60-3.50				2.30-2.25				1.45-1.40		
	6.50- 6.00				3.50-3.40				2.25-2.20				1.40-1.35		
	6.00- 5.75				3.40-3.30				2.20-2.15				1.35-1.30		
	5.75- 5.50				3.30-3.20				968	ZnCrO <sub>4</sub>	9.50		1.30-1.25		
	5.50- 5.25				3.20-3.10				2.15-2.10				1.25-1.20		
	5.25- 5.00				3.10-3.00				2.10-2.05				1.20-1.15		
	5.00- 4.90				3.00-2.95			407	FeCl <sub>3</sub>	5.90			1.15-1.10		
171	5CaO·3Al <sub>2</sub> O <sub>3</sub>	2.44							2.05-2.00				1.10-1.05		
	4.90- 4.80				2.95-2.90				2.00-1.95				1.05-1.00		
	4.80- 4.70			502	Mg <sub>2</sub> Ca	3.14			1.95-1.90				1.00- .90		
	4.70- 4.60				2.85-2.80				1.90-1.85				.90- .80		
								672	KF	3.08					
	4.60- 4.50				2.80-2.75			846	Na <sub>2</sub> HPO <sub>3</sub> ·5H <sub>2</sub> O	1.54	4.23				
								170	3CaO·Al <sub>2</sub> O <sub>3</sub>	1.54	4.05		.80-		
	4.50- 4.40				2.75-2.70										
				752	Ag <sub>2</sub> CO <sub>3</sub>	2.27									

SUPPLEMENTARY GROUP INDEX 2.70-2.65

No.	Compound	1st line	2nd line	3rd line	No.	Compound	2nd line	1st line	3rd line	No.	Compound	3rd line	1st line	2nd line
171	5CaO·3Al <sub>2</sub> O <sub>3</sub>	2.68	4.90	2.44	354	CuCl <sub>2</sub> ·2NH <sub>4</sub> Cl·2H <sub>2</sub> O	2.68	5.5	2.75	138	BiO <sub>2</sub> C <sub>10</sub> H <sub>7</sub>	2.67	20.0	9.9
502	Mg <sub>2</sub> Ca	2.65	2.87	3.14	314	Cr <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	2.68	4.75	9.2	120	Ba(CNS) <sub>2</sub> ·2H <sub>2</sub> O	2.66	7.7	3.4
752	Ag <sub>2</sub> CO <sub>3</sub>	2.65	2.73	2.27	544	MgSO <sub>4</sub> ·7H <sub>2</sub> O	2.66	4.22	5.9	532	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	2.69	6.7	2.94
423	Fe <sub>2</sub> O <sub>3</sub>	2.69	2.51	1.84	533	MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O	2.69	4.28	2.93	566	Mn <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2½H <sub>2</sub> O	2.67	4.80	3.00
765	Ag <sub>3</sub> PO <sub>4</sub>	2.68	2.45	1.66	448	Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>	2.65	3.48	5.8	682	KNO <sub>3</sub>	2.66	3.77	3.03
968	ZnCrO <sub>4</sub>	2.67	2.14	9.5	133	BiOCl	2.67	3.45	7.4	650	K	2.65	3.75	2.16
407	FeCl <sub>3</sub>	2.68	2.08	5.9	111	BaO <sub>2</sub>	2.68	3.37	2.11	829	NaHC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	2.67	2.97	2.45
846	Na <sub>2</sub> HPO <sub>3</sub> ·5H <sub>2</sub> O	2.67	1.89	1.54	907	TeCl <sub>2</sub>	2.69	3.24	4.29	792	Na <sub>2</sub> CO <sub>3</sub> ·1H <sub>2</sub> O	2.67	2.76	2.37
170	3CaO·Al <sub>2</sub> O <sub>3</sub>	2.68	1.90	1.55	879	Na <sub>2</sub> C <sub>5</sub> H <sub>2</sub> O <sub>3</sub> N <sub>4</sub> ·H <sub>2</sub> O	2.66	3.17	4.72	481	LiOH	2.67	2.75	4.35
672	KF	2.66	1.88	3.08	936	SnSO <sub>4</sub>	2.67	3.08	2.10	442	FeS	2.65	2.06	2.98
					48	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	2.67	3.06	3.81	524	Mg <sub>3</sub> N <sub>2</sub>	2.66	1.76	2.12
					866	N <sub>2</sub> SO <sub>3</sub> ·7H <sub>2</sub> O	2.66	2.87	4.26					
					315	Cr <sub>2</sub> O <sub>3</sub>	2.67	1.67	2.47					



Group 2, 95-2.90

No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line	No.	Compound	3rd line	4th line
	20.00-15.00				4.40-4.30				2.80-2.75				1.90-1.85		
	15.00-12.00				4.30-4.20			925	Sn	2.01			1.85-1.80		
	12.00-10.00			818	NaIO <sub>3</sub>	3.19		178	CaC <sub>2</sub> II	1.95		779	NaN <sub>3</sub>	2.42	
	10.00- 9.00				4.20-4.10				2.75-2.70				1.80-1.75		
	9.00- 8.50				4.10-4.00			801	Na <sub>2</sub> CrO <sub>4</sub>	4.09		396	In <sub>2</sub> O <sub>3</sub>	1.52	
	8.50- 8.00			465	Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	3.61			2.70-2.65				1.75-1.70		
	8.00- 7.50				4.00-3.90				2.65-2.60				1.70-1.65		
	7.50- 7.00				3.90-3.80				2.60-2.55			303	CsCl	4.11	
	7.00- 6.50				3.80-3.70			795	NaHCO <sub>3</sub>	3.48			1.65-1.60		
640	P <sub>2</sub> S <sub>5</sub>	4.90		152	CdCO <sub>3</sub>	1.83		918	Th	1.79			1.60-1.55		
	6.50- 6.00				3.70-3.60				2.50-2.45				1.55-1.50		
600	HgSO <sub>4</sub> ·2HgO	5.5		93	Ba(ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	2.14		685	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	2.32			1.50-1.45		
	6.00- 5.75				3.60-3.50				2.45-2.40				1.45-1.40		
	5.75- 5.50				3.50-3.40				2.40-2.35				1.40-1.35		
	5.50- 5.25			715	C <sub>16</sub> H <sub>8</sub> O <sub>2</sub> N <sub>2</sub> (SO <sub>3</sub> K) <sub>2</sub>	3.00			2.35-2.30				1.35-1.30		
877	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	2.84			3.30-3.20				2.30-2.25				1.30-1.25		
	5.25- 5.00			797	NaClO <sub>3</sub>	1.76			2.25-2.20				1.25-1.20		
	5.00- 4.90				3.20-3.10				2.20-2.15				1.20-1.15		
	4.90- 4.80				3.10-3.00			782	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O	4.40			1.15-1.10		
	4.80- 4.70				3.00-2.95				2.15-2.10				1.10-1.05		
	4.70- 4.60				2.95-2.90				2.10-2.05				1.05-1.00		
	4.60- 4.50				2.90-2.85				2.05-2.00				1.00- .90		
	4.50- 4.40				2.85-2.80				2.00-1.95				.90- .80		
786	(C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> ) <sub>2</sub> - BONa	3.45							1.95-1.90				.80-		

## SUPPLEMENTARY GROUP INDEX 2.95-2.90

[illegible]



have been measured and tabulated. One opens the index book at the major group determined by the strongest line, turns to the subgroup determined by the second strongest line, and sees whether any of the lines of the unknown check lines in this subgroup. (This can be done at a glance since, of the subgroups which are occupied, the largest contains only seven patterns and most of them contain only one.) If the unknown is a single substance, the third strongest line will check and the pattern will have been located. However, if the unknown is a mixture of phases and if the second strongest line of the pattern happens to be the strongest line of the second component, the pattern will not have been found and one proceeds by using the third strongest line of the unknown pattern to determine the subgroup, and so on. When a match is found, the lines of the unknown coinciding with the standard are noted, as are also any intensity variations which would indicate superpositions of lines. The remaining unidentified lines of the unknown are then treated in the standard manner.

TABLE I. X-RAY DIFFRACTION DATA

<i>d</i> <sup>a</sup>	<i>I</i> <sup>b</sup>	<i>I</i> / <i>I</i> <sub>1</sub> <sup>c</sup>
4.95	8	0.13
4.08	25	0.40
3.89	20	0.32
3.58	17.5	0.28
2.91	62.5	1.00
2.73	40	0.64
2.47	15	0.24
2.16	7	0.11
2.11	5	0.08
2.03	15	0.24
1.94	10	0.16
1.79	15	0.24
1.72	1	0.02
1.68	2	0.03
1.64	6	0.10
1.61	12.5	0.20

<sup>a</sup> *d* = interplanar spacing measured in Angstrom units.  
<sup>b</sup> *I* = intensity of the diffraction line (arbitrary units).  
<sup>c</sup> *I*<sub>1</sub> = intensity of the strongest line.

If the constituent corresponding to the strongest line of the unknown pattern is not contained in the file, or if the strongest line should happen to be so by virtue of the superposition of two lines, neither of which is the strongest line of any component present in a mixture, one will not find a match in the major group determined by the strongest line of the unknown pattern, so he must proceed by using the second strongest line to determine the major group, and so on. One cannot fail to find any or all components of a mixture which exists in the reference file. If the pattern is not found in the file, then even in this case one has obtained considerable negative information about the unknown.

Use of System in Identifying Unknowns

Probably the easiest way to become acquainted with the details of the system is to follow through the determinations of a few unknowns. For this purpose, three sections of the index book (Figures 2, 3, 4) have been chosen to be reprinted. (The complete index book is not reprinted here because it requires 462 pages, but it can, of course, be easily tabulated from the pattern data given.)

In working with a real unknown, one cannot, in general, tell by simply looking at the pattern whether it represents a single substance or a mixture, nor is it necessary to know this. However, for simplicity the illustrations are picked from different types of cases.

A. A SINGLE COMPONENT. Assume that the measurements of the pattern have been recorded as in Table I.

The three strongest lines in order of decreasing intensity are 2.91, 2.73, 4.08. Turn to the index book to group 2.95–2.90 (Figure 4) and look in subgroup 2.75–2.70. One finds that sodium chromate, pattern No. 801, has a third line at 4.09, which is also the third most intense line of the unknown. Then turn to pat-

tern No. 801 and observe that within experimental error all positions and relative intensities check and there are no lines of either pattern not accounted for. The conclusion is that the unknown contains sodium chromate.

B. MIXTURE OF TWO SUBSTANCES (no superposed index lines). The data of such an unknown are reproduced in Table II.

TABLE II. X-RAY DIFFRACTION DATA

<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
4.65	6	1.82	4
3.79	12.5	1.75	30
3.28	30	1.71	2
2.93	50	1.63	1
2.67	20	1.58	10
2.52	50	1.54	1.5
2.32	50	1.50	15
2.18	15	1.465	1.5
2.07	2	1.430	6
1.97	6	1.406	10
1.86	10	1.372	10

Turn to group 2.95–2.90 (Figure 4) and to subgroup 2.55–2.50 and find that there is no compound with a third line corresponding to any of the lines of the unknown. Turn next to subgroup 2.35–2.30 and again find no match. Turn next to subgroup 3.30–3.20 and observe that sodium chlorate, pattern No. 797, has a third line at 1.76. Since there is a line at 1.75 in the unknown pattern, compare the data of sodium chlorate, pattern No. 797, with that of the unknown and list the relative intensities of the identified lines. This gives Table III in satisfactory agreement with sodium chlorate, pattern No. 797.

TABLE III. X-RAY DIFFRACTION DATA

<i>d</i>	<i>I</i>	<i>I</i> / <i>I</i> <sub>1</sub>
4.65	6	0.12
3.79	12.5	0.25
3.28	30	0.60
2.93	50	1.00
2.67	20	0.40
2.18	15	0.30
2.07	2	0.04
1.97	6	0.12
1.82	4	0.08
1.75	30	0.60
1.63	1	0.02
1.58	(10)	(0.20)
1.54	1.5	0.03
1.50	(15)	(0.30)
1.465	1.5	0.03
1.430	6	0.12

The identification of one compound of the mixture is thus established. The strongest of the remaining lines is at 2.52; hence turn to group 2.55–2.50 (Figure 2), subgroup 2.35–2.30, and note the compound cupric oxide, pattern No. 372, with a third line at 1.86. Referring to the data of cupric oxide, pattern No. 372, note that all the remaining lines of the unknown are accounted for in position. List the relative intensities, Table IV.

TABLE IV. X-RAY DIFFRACTION DATA

<i>d</i>	<i>I</i>	<i>I</i> / <i>I</i> <sub>1</sub>
2.52	50	1.00
2.32	50	1.00
1.86	10	0.20
1.71	2	0.04
1.58	(10)	(0.20)
1.50	(15)	(0.30)
1.406	10	0.20
1.372	10	0.20

These are seen to be in satisfactory agreement with the cupric oxide data. Since all the diffraction lines of the unknown have been satisfactorily accounted for, the qualitative compound analysis of the mixture is complete.

C. MIXTURE OF TWO COMPONENTS (superposed lines). The data for the unknown are recorded in Table V.

TABLE V. X-RAY DIFFRACTION DATA

<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
4.90	2	1.309	4
3.68	4	1.274	2
2.96	7	1.256	3
2.69	25	1.220	1
2.52	50	1.189	2
2.43	1	1.160	2
2.21	7	1.140	2
2.08	8	1.120	1
1.84	15	1.103	1
1.69	17.5	1.089	2
1.61	15	1.054	2
1.480	25	1.040	1
1.450	10		



Turn to group 2.55–2.50 (Figure 2), subgroup 2.70–2.65, and find no compound listed with a third line corresponding to any of the lines of the unknown. Turn to subgroup 1.50–1.45 and find iron ferrite (ferrosoferric oxide), pattern No. 426, with a third line at 1.62. Compare the data of pattern No. 426 with the data of the unknown. On listing the relative intensities of the identified lines (Table VI), it is seen that the intensity of line 2.52 is decidedly too high, which suggests the possibility of a superposition of lines.

TABLE VI. X-RAY DIFFRACTION DATA

<i>d</i>	<i>I</i>	<i>I</i> / <i>I</i> <sub>1</sub>
4.90	2	0.04
2.96	7	0.14
2.52	50	1.00
2.43	1	0.02
2.08	8	0.16
1.69	17.5	0.35
1.61	15	0.30
1.480	25	0.50
1.274	2	0.04
1.120	1	0.02
1.089	2	0.04
1.054	2	0.04

Therefore include line 2.52 along with the remaining unidentified lines. Inspection shows that the intensity of the superposed line on 2.52 of iron ferrite is about as strong as line 2.68. However, group 2.55–2.50, subgroup 2.70–2.65, gives no check, while group 2.70–2.65, subgroup 2.55–2.50, lists ferric oxide, pattern No. 423, with a third line at 1.84. Comparing the data of ferric oxide, pattern No. 423, with the data of the unknown, it is found that the positions of the ferric oxide lines check with all of those of the remaining unidentified lines of the unknown as well as with three of the lines which had already been checked with the iron ferrite pattern. Thus there are superpositions of lines at three positions in the unknown pattern. In order to show conclusively that the unknown is a mixture of ferric oxide and iron ferrite, it is necessary to account satisfactorily for the relative intensities of the lines of the unknown pattern. Since line 2.69 is not a superposed line, its intensity is due entirely to ferric oxide, and to get the value of the absolute intensities of all other ferric oxide lines of the unknown, it is only necessary to multiply the intensity of line 2.69 by the known relative intensities of ferric oxide as given in pattern No. 423. This is done in Table VII.

TABLE VII. X-RAY DIFFRACTION DATA

<i>d</i>	<i>I</i>	<i>I</i>
3.68	0.18 × 25 =	4.5
2.69	1.00 × 25 =	25
2.52	0.75 × 25 =	19
2.21	0.18 × 25 =	4.5
1.84	0.63 × 25 =	16
1.69	0.63 × 25 =	16
1.61	0.13 × 25 =	3
1.480	0.50 × 25 =	12.5
1.450	0.50 × 25 =	12.5
1.309	0.18 × 25 =	4.5
1.256	0.13 × 25 =	3
1.189	0.08 × 25 =	2
1.160	0.05 × 25 =	1
1.140	0.13 × 25 =	3

Then subtract these computed absolute intensities from those of the total unknown pattern (Table VIII). The resulting data must agree with those of iron ferrite, if the identification of the unknown is to be considered complete. This is found to be the case. The low intensity in the case of line 1.48 can be explained by the fact that this line in the unknown pattern is a partially superposed line, and the intensity as read is not the sum of the intensities of the lines. The case could never exist where this phenomenon would cause the intensity of a line to be calculated too high.

It is worth while to point out an alternative method of identifying a mixture of the above type by making use of the Supplementary Group Index. If one inadvertently fails to recognize the anomalously high intensity of the spacing 2.52 for the identified iron ferrite pattern and proceeds to identify the second phase in the usual manner, he might easily neglect to reconsider the spacing 2.52 (inasmuch as the spacing has already been identified as the most intense line of iron ferrite) and consequently fail to locate the second phase. In that

event, upon looking in group 2.70–2.65 in the standard manner, one fails to identify the remaining lines. He then refers to supplementary group 2.70–2.65 and finds listed along with 2.68 and 1.84 the line 2.51 which also occurs in the unknown pattern. The ferric oxide pattern would then be checked. The Supplementary Group Index in general is useful when for any reason the strongest line of a pattern is overlooked and one is attempting to identify a pattern from its second or third strongest lines. While the illustrations have been limited to mixtures of only two unknowns, no new situation will be encountered in mixtures of three or more components. It has been found from experience in this laboratory that it is practical to use this method of analysis for mixtures with as many as four or five components. However, the ease of analysis becomes less as the number of components increases.

Apparatus and Technic

The x-ray literature describes many types of apparatus for diffraction work (1, 2, 4, 6, 7, 10). The type to be used in any particular case depends on the kind of data desired and the accuracy necessary. A completely equipped x-ray laboratory which could handle all the x-ray technics for diverse purposes would require a large variety of apparatus. However, for the particular purpose of chemical analysis under discussion in this article, a satisfactory equipment and experimental procedure which is sufficiently accurate and at the same time economical will be described.

The diffraction unit most used in this laboratory is the G. E. multiple diffraction unit, Type VWC, Form E, as described by Davey (3) (Figure 5). (The production of this particular type of x-ray unit has been suspended at the present time, though other powder diffraction units are commercially available.) This unit consists of a transformer, x-ray tube with a molybdenum target, and cameras. Twelve slits 0.05 × 1.25 cm. (0.02 × 0.5 inch), located around the circumference of the cylinder containing the x-ray tube, define the x-ray beams. There is a switch-board holding the operating switches, meters, filament current stabilizer, a water pressure switch, and an overload circuit breaker. In this laboratory there have been added a recording milliammeter, which gives a record of the tube current during the exposure; a time switch, by which an exposure can be stopped at a predetermined time; and a temperature switch, which shuts off the voltage if the temperature of the cooling water reaches about 38° C. (100° F.). The G. E. quadrant cassettes of 20.32-cm. (8.00-inch) radius (Figure 6) are used. A slight modification of these cameras makes it possible to record the diffraction lines on both sides of the beam. This produces a symmetrical pattern, which enables an accurate location of the setting of the primary beam on the zero of the measuring scale (Figure 1). In order to obtain a more uniform pattern, the specimen tube is rotated during the exposure. The power for rotating the specimen is supplied by an electric clock motor and is transmitted by a silk fish-line belt. A zirconium dioxide filter about 0.04 cm. (0.016 inch) thick is placed in front of the film to absorb the MoKβ radiation. (These filters are supplied by the Patterson Screen Company, Towanda, Pa.) Double-emulsion x-ray film 4.76 × 40 cm. (1.875 × 16 inches), costing about 7.5 cents each is used. A fluorazure intensifying screen (also supplied by the Patterson Screen Company) is placed immediately behind the film. The specimens are loaded in powder form in Pyrex capillary tubes 0.04-cm. (0.016-inch) inside diameter (measured with a No. 78 drill) and 0.06-cm. (0.025-inch) outside diameter (measured with a No. 22 U. S. standard wire gage). These tubes can be

TABLE VIII. X-RAY DIFFRACTION DATA

<i>d</i>	<i>I</i>	<i>I</i> / <i>I</i> <sub>1</sub>
4.90	2	0.07
2.96	7	0.23
2.52	31	1.00
2.43	1	0.03
2.08	8	0.26
1.69	1.5	0.05
1.61	12	0.39
1.480	12.5	0.40
1.274	2	0.07
1.220	1	0.03



readily made in large quantities. A plug of absorbent cotton about 0.1 cm. (0.04 inch) long is placed in the center of the tube. The samples are then loaded on either side of the central plug for a distance of 1 cm. (about 1 mg.) in a manner similar to that used in loading melting point tubes. Piano wire serves well as an aid in packing because it does not buckle and break the tube. After the sample is packed into the tube, another cotton plug is inserted and the ends of the tube are sealed in a flame. Brittle substances can be prepared for loading by grinding in an agate mortar. Samples of metals can be obtained by filing with a clean file. It has been found helpful to have available various dental tools for the purpose of obtaining samples of small inclusions in nonhomogeneous materials. A desiccator box equipped with glass top and rubber sleeves is more convenient for loading hygroscopic substances than loading under a protective liquid. Samples which contain elements of high atomic number should be diluted with an amorphous material such as flour or charcoal to decrease the absorption of the radiation. In general, about 200-mesh is a satisfactory powder size to use. The preparation and loading of a sample can usually be accomplished in 5 minutes or less.

The loaded tube is inserted in the pulley of the camera and secured by Picein wax. The camera is then placed on the diffraction unit and exposed for 6 hours at 30,000 volts and 20 milliamperes. The unit holds twelve cameras, so that 24 specimens may be exposed simultaneously. (When an analysis is desired in the least possible elapsed time, use of copper radiation and a different type of camera would require an exposure time of only about 15 minutes. This technic would not permit the simultaneous exposure of 24 specimens, however.) The exposed films are then developed as a batch in standard x-ray developer for 5 minutes at 18°C. (65° F.), fixed in x-ray hypo for about 12 minutes, washed in running water for 20 to 30 minutes, and dried in a

film dryer. The drying takes about half an hour. The developed film, or pattern, is now ready to be measured.

TABLE IX. TIME STUDY OF OPERATIONS

	Time Man-minutes
Preparation of specimens and filling of tubes (24 specimens)	120
Loading cameras, mounting specimen (24 specimens)	45
Removing cameras after exposure and filing specimen (24 specimens)	30
Darkroom operation (24 specimens)	20
Labeling and filing negatives (24 specimens)	30
Total	245
Preparation of pattern, average time per specimen	10
Measurement of pattern, average time per specimen	10-15
Identification of pattern, average time per specimen	5-15
Total man-minute time for analysis and permanent record, per specimen	25-40

The pattern is placed symmetrically in the measuring scale (Figure 1) and the positions of the different lines are read off in the order of decreasing Å. spacings. The scale divisions beginning at 20 Å. are 20, 15, 12, 10, 9; every 0.5 Å. from 9 to 6; every 0.25 Å. from 6 to 5; every 0.1 Å. from 5 to 3; every 0.05 Å. from 3 to 2; and every 0.01 Å. from 2 to 0.55.

The next step is to record the intensities of the lines with the aid of an intensity scale. The pattern is placed on top of the intensity scale, and the combination is viewed by eye in transmitted light. A match is then sought between the diffraction line and the standard lines of the intensity scale. The complete data of the diffraction pattern are thus recorded, giving the interplanar spacing and numerical intensity of each line.

The preparation of an intensity scale must be carried out very carefully. However, it need be done only once if the scale is protected from wear by sealing in a Cellophane envelope. (The diffraction patterns themselves can well be filed in Cellophane envelopes.)

While the pattern consists of diffraction lines formed by x-ray beams of very different intensities but of the same exposure time, the intensity scale can, by virtue of the reciprocity relation which holds for x-rays, be constructed by using an x-ray beam of constant intensity and varying the exposure times. The value of the intensity for each step of the intensity scale is therefore proportional to the time of exposure used for that step.

In order to have a beam of  $\text{MoK}\alpha$  radiation of intensity comparable with the powder reflections, a calcite crystal monochromator was used in conjunction with an absorber further to reduce the intensity of the beam. The exposure times were determined to one-third second by a shutter system. The film was mounted on a drum which was turned by a 400-to-1 reduction gear, for the purpose of easily spacing the intensity steps. The secondary voltage was kept constant at about 25 kilovolts to within 0.5 per cent. The tube current was maintained constant by a stabilizer. The shortest exposure to produce a barely visible mark on the film was 10 seconds. This blackness was arbitrarily chosen to represent unit intensity. The longest exposure was 3250 seconds, corresponding to an intensity of 325. The steps of the intensity scale are such that easily observable differences in blackness exist between adjacent intensity marks, and are as follows: 1, 2, 4, 6, 8, 10, 15, 20, 30, 50, 75, 125, 175, 250, 325. The width of the intensity marks is made approximately the same as that of the diffraction lines.

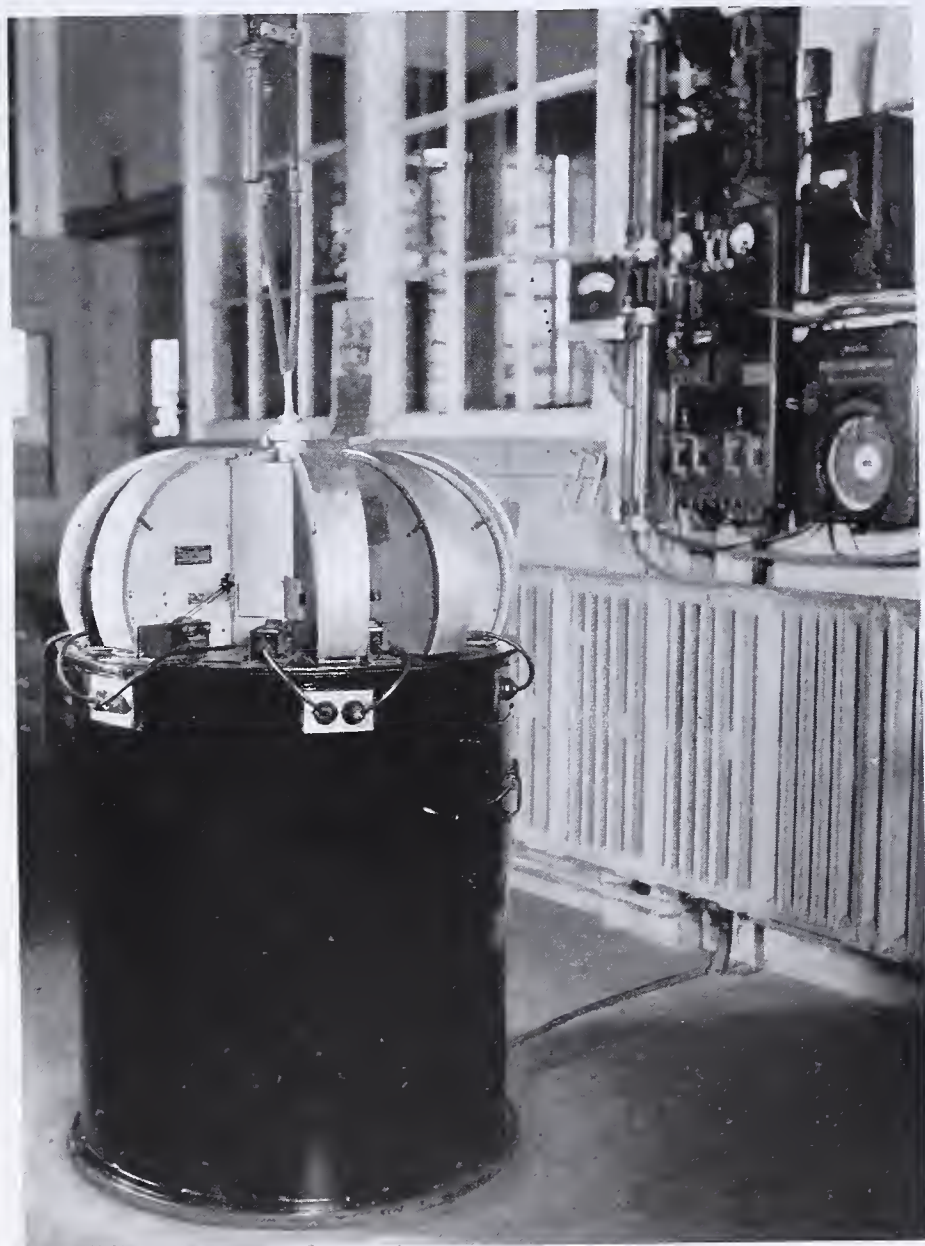


FIGURE 5. DIFFRACTION APPARATUS AND CONTROL BOARD



A fair idea of the approximate expense and time involved in carrying out analysis by the x-ray method can be obtained from data based on actual operation in this laboratory.

If only one specimen were run through instead of 24 at a batch, the time for preparation of the pattern would be about 25 minutes instead of 10.

TABLE X. COST OF SUPPLIES

	Cents
X-ray tube (\$225 per tube, average life 12,000 hours' operation) per specimen	0.5
Darkroom supplies	0.7
X-ray film	3.7
Specimen tube	2.0
Power	0.3
Total cost of supplies per specimen	7.2

The expense of the analysis is almost entirely due to the labor involved (Table X).

### Accuracy of the Data

**SPACING MEASUREMENTS.** In the experimental technic as given, the error of measurement of spacings increases in a smooth curve from  $\pm 0.001 \text{ \AA.}$ , at  $1.0 \text{ \AA.}$ , through  $\pm 0.01 \text{ \AA.}$  at  $3.5 \text{ \AA.}$  to  $\pm 0.06 \text{ \AA.}$  at  $8.0 \text{ \AA.}$  Higher accuracy than this, of course, could be attained by modern precision x-ray methods, but only at the expense of the ease and speed of making the measurements. The use of  $\text{MoK}\alpha$  radiation and a large camera radius of 20.32 cm. (8.00 inches), as described, makes possible the rapid measurement of the position of the lines on a scale, whereas use of a small precision camera and a comparator is not only tedious but also makes the measurement of weak lines very difficult. In order to secure the accuracy obtained, all cassettes are calibrated with sodium chloride. Since all films are treated under standardized conditions, the effect of film shrinkage is absorbed in the sodium chloride calibration. In 310 cases (the starred compounds) an independent check on the accuracy of the measured spacings was afforded by calculation of the spacings from published data listed by Wyckoff (10) and Ewald and Hermann (5). The agreement was within the experimental error. Each of the 1000 patterns was measured independently by two different observers.

**INTENSITY MEASUREMENTS.** The most objective method of measuring the intensities would be to use the microphotometer or densitometer. However, one year's experience with a direct comparison intensity scale has shown that it is sufficiently accurate for use with the classification system. It has the advantages of being rapid and easy to use. Weak lines can be measured in this way when they would be difficult to record with a microphotometer. The steps of the intensity scale are such that successive differences in blackness can easily be recognized. In use, one decides only whether the intensity of the diffraction line lies closer to one of two adjacent pairs of intensity marks, or lies nearer the mean. To check the accuracy of the intensity data, each of the 1000 patterns was read by two independent observers. The agreement was found to be within the steps of the intensity scale. It has been thoroughly tested that the relative intensities of the lines of a pattern remain essentially unchanged, even though the absolute strength of the pattern be different—for instance, because of different exposure times or amount of diffracting material in the tube. One can obtain on a single film the equivalent of two different exposures by covering half the x-ray film lengthwise with a suitable thickness of aluminum foil.

In order to attach a physical meaning to the seemingly arbitrary intensity values, microphotometer tracings were made of the intensity scale itself and of a number of sodium chloride films, for which the time of exposure and the con-

centration of sodium chloride were varied. This work showed that the use of the intensity scale eliminates the background and gives intensity values proportional to the peak intensities of the diffraction lines. The relative intensities as listed in the tables of data refer to intensities of the diffraction lines from rotated powdered specimens.

Besides the relative intensities, the values of the intensity of the three strongest lines of each compound are included in the tabulated data in order to have a measure of the absolute strength of the diffraction pattern. This information frequently permits a rough estimate of the sensitivity of detec-

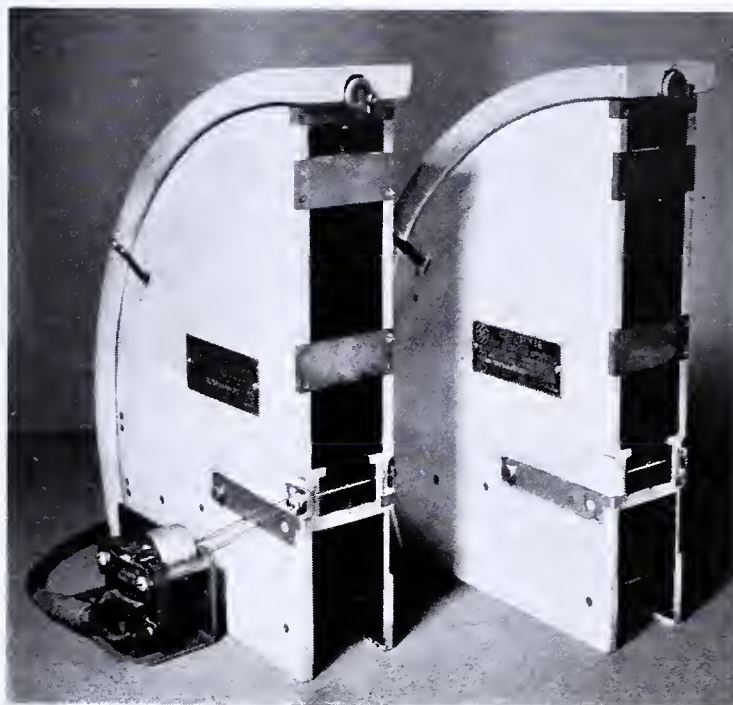


FIGURE 6. FILM CASSETTES WITH SPECIMEN TUBE AND ROTATING DEVICE

tion of a compound in a mixture. In using the intensity data, one should bear in mind that the agreement between the tabulated relative intensities and those determined by the analyst for his film is only a semiquantitative one. While the recorded data for the 1000 compounds were obtained with  $\text{MoK}\alpha$  radiation, it is possible to use the same data for  $\text{CuK}\alpha$  radiation, provided due precautions are taken to reduce the effect of absorption.

### Sources and Reliability of Standards

The majority of the 1000 standards listed in this article have not been subjected to a complete chemical analysis. At The Dow Chemical Company, the patterns of a considerably larger number of substances have been entered in the index book and file. Whenever any one of these patterns is used as a standard, its reliability is invoked and, if questioned, is closely examined. However, to permit testing the usability of the classification system and x-ray method of chemical analysis, 1000 substances were selected whose compositions are thought to be reasonably certain.

The starred patterns are those for which it was possible to check all the lines of the pattern with published crystal structure data. This comprehensive check included the calculation of the spacings, the indexing of the lines, and the application of space group criteria. Since, in general, when a crystal structure investigation is made, the chemical formula of the substance must be definitely known, there is little reason to question the reliability of the starred patterns. There are 310 such patterns. Unfortunately, crystal structure data



are lacking for most of the balance of the 1000 patterns. Compounds rated chemically pure were obtained from Eimer & Amend, Merck & Co., Inc., Mallinckrodt Chemical Works, E. H. Sargent and Company, General Chemical Co., Vanadium Corporation of America, G. Frederick Smith Chemical Co., Central Scientific Company, Eastman Kodak Company, and The Dow Chemical Company. When it was not possible to obtain the desired compounds in a c. p. grade, the available grade was used. The less stable hydrates of a sizable group of compounds were prepared in this laboratory, and the degree of hydration was checked gravimetrically. In addition, about 50 compounds not commercially available were synthesized.

It is probable that a small number of cases exist among the unstarred patterns for which the data do not represent the exact formula as given. An idea of the type and extent of the errors to be expected can be obtained from a consideration of the results in those cases where a check with the crystal structure data was possible. Of the 342 cases so investigated, in 14 cases the degree of hydration was incorrectly given by the label on the reagent bottle, the diffraction pattern obtained being that of a different hydrate or of a mixture of hydrates. Seven cases resolved themselves as a mechanical mixture of the labeled substance and an impurity, and four cases as polymorphic mixtures of the same chemical substance. In seven instances, the diffraction pattern experimentally obtained differed completely from the data as published in the crystal structure literature.

### Field of Application of X-Ray Diffraction in Chemical Analysis

It is well known that there are definite limitations to the field of application of the x-ray method of analysis, but the important question is as to the range of usefulness left when these things are taken into account. The method is limited in the first place to solids, and secondly to those solids which are crystalline, meaning by crystalline simply those substances which give a pattern. The only way to determine whether or not a material will give a pattern is to subject the material to x-ray diffraction. It has been found experimentally that about 5 per cent of the solid inorganic chemical substances are essentially amorphous and give no pattern by which they could be identified.

A considerable number of other substances give such weak patterns that, while they could be identified if they were the only constituents present, they might escape detection if they were mixed with something else. Depending to some extent on what the substances are mixed with, some would show if they represented less than 1.0 per cent of the material being examined, but many would not show at less than 10.0 per cent and some would not show plainly even when as much as 50.0 per cent was present. The magnitude of this figure can be estimated after the pattern has been obtained, but cannot be told beforehand. Still another weakness of the method is that appreciable percentages of elements may be present in solid solution without changing the pattern enough to be detected, at least without special technic.

Thus, while certainty of analysis is one of the valuable features of the x-ray method, this certainty applies only to what the pattern does show and not to what it does not show. If, for instance, one obtains the pattern of manganese chloride dihydrate it is certain that manganese chloride dihydrate is present. However, it is not certain that there is not a small amount of a more or less amorphous material mixed with it, nor that there is not in solid solution in the manganese chloride a substance which does not greatly change the characteristics of the manganese chloride pattern.

For these reasons the x-ray method is not independent and

cannot, in general, stand alone as a means of chemical analysis. The x-ray data must be combined with other data for complete information. The combination of spectroscopy and x-ray diffraction is very fortunate, since they supplement each other's deficiencies by giving entirely different types of information about the same substance. In the arc or spark, the material is broken up into its elements, so that they show regardless of the state in which they were present, while the x-ray, without so much as changing the temperature of the material, records the existing chemical and physical state. The spectrograph is also sensitive in the region of small percentages, where the x-ray is not.

Installation of x-ray diffraction in the laboratory does not, in general, displace other technics, but gives the power to get more information or to obtain information under peculiarly difficult conditions. A practical procedure is to make a survey analysis before other work is attempted. In those cases in which the information obtained is sufficient, it does eliminate other work.

In the field of identification, the merits of x-ray diffraction analysis are sometimes compared with those of microscopic examination. The technics involved and the scientific principles invoked are different. The microscope is much more sensitive than the x-ray to the presence of small percentages of substances, and to amounts of sample of less than 0.1 mg., which is about the practical limit for the x-ray method. It is equally true that the x-ray is much more suited to the general problem of determining the chemical state and composition of the main components of an unknown. The x-rays are less affected by superficial differences, since they analyze the body of the substance. Furthermore, the interpretation of the diffraction pattern is direct. The experimental technic involved can be rapidly acquired. A further advantage of the x-ray method is that no special requirements are imposed upon the form of the specimen. It seems fair to say that, in general, no other single method will yield compound analysis of solids so reliably and economically.

The field of application of x-ray in chemical analysis might be summarized in a general way by saying that, wherever it is necessary to maintain an analytical laboratory, an invaluable supplementary technic will be found in x-ray diffraction. The following are some of the unique features which have been found of practical importance in this laboratory:

1. The substances present show in their true state of chemical combination.

The analysis of reaction mixtures is a good illustration of the application of this feature. The analysis of the residue or slag of a high-temperature reaction in this way shows which components of the charge react, and what the equation of the reaction is. For example, it is desired to determine whether the compounds calcium carbide and calcium silicide will react. About a gram of the two in molecular proportions is mixed and ground, and the mixture is heated to 1500° C. in a small electric vacuum furnace. Before heating, the mixture is a dark powder whose x-ray pattern is the superposition of the calcium carbide and calcium silicide patterns. After heating, the powder looks the same as before, but the x-ray pattern shows only silicon carbide. One concludes with certainty that reaction has taken place according to the equation



The entire experiment is done with a minimum of expense and time.

A problem which resisted the usual chemical methods of attack was that of the chemicals added to molding sand to inhibit the oxidation of magnesium alloys on casting. A single compound such as ammonium fluoride or ammonium borofluoride may be added to the sand, but reactions begin to take place immediately. The question therefore arises as to what chemicals are actually present in the sand and which ones are actually effective in inhibiting oxidation. The chemical analysis for the ammonium radical present gave no hint as to the



various ammonium compounds present; but the x-ray patterns showed that as many as six different ammonium compounds are present in the sand after using it awhile, and, by identifying them separately, showed what reactions were taking place and which agents were stable and which effective in inhibiting oxidation. By setting up standard mixtures with a range of concentrations of the various compounds involved—ammonium fluoride, ammonium acid fluoride, ammonium fluosilicate, ammonium borofluoride, ammonium chloride, ammonium sulfate, boric acid, and sulfur—it was possible to make a semiquantitative analysis on the basis of the relative intensities of the diffraction lines. The ability of the x-ray to recognize these compounds separately though mixed together was thus very valuable.

A point in connection with this problem which illustrates the fact that the x-ray pattern serves as a unique identification of a substance was that besides the compounds in the sand which were definitely identified, there occurred a substance giving a pattern which could not be identified. The substance was temporarily called X, and it was possible to determine the approximate per cent present in the sand and that it was effective in inhibiting oxidation even before it was isolated and identified by chemical methods. If the file and index of patterns had been available 5 years ago when this problem was investigated, the pattern X would have been identified immediately.

2. The analysis is conclusive, even though only minute amounts of material are available. This is especially valuable for corrosion products from small pits or surface attacks. Identification of small deposits and sediments can also be readily accomplished.

3. Substances are analyzed directly in their "as received" state and are not destroyed.

4. Different crystalline phases, states of oxidation or hydration, and physical state are observable. The ability to determine the degree of graphitization of carbon, or to distinguish quartz and cristobalite, or the high- and low-temperature forms of compounds—e. g., dicalcium silicate, etc.—is frequently important. The patterns of the various oxides of an element—e. g., ferrous oxide, ferric oxide, ferrosferric oxide—are distinct from each other and, of course, from that of the element itself. The state of hydration of calcium chloride as a function of process and also as a function of position in the individual clusters of crystals can be determined, and in other cases the existence of water as water of crystallization can be detected.

5. As has been discussed rather fully in the present article, the process of preparing the specimen and obtaining the x-ray pattern is simple and economical.

6. A permanent record of the original data is always on file in the form of the diffraction pattern.

These features, which have been enumerated, are of obvious importance and would make x-ray diffraction valuable in many analysis problems, even though an easy method of indexing the patterns were not possible. However, the classification system greatly facilitates the use of x-rays in these cases and extends its field of application to include complete unknowns.

At the present stage of development, x-ray diffraction gives a qualitative or semiquantitative analysis. The accuracy possible varies widely in different cases, but in a favorable case allows a determination to within about 5 per cent of the amount present.

Future technical improvements will undoubtedly greatly increase the accuracy attainable as well as the scope of the x-ray diffraction method of analysis.

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[Tables XI and XII follow, pages 467 to 512, inclusive]

TABLE XI. INDEX TO POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES

Pattern No.	Name	Formula	Pattern No.	Name	Formula
1	Aluminum	Al	30	Ammonium carhamate	NH <sub>4</sub> CO <sub>2</sub> NH <sub>2</sub>
2	bromide	AlBr <sub>3</sub> ·6H <sub>2</sub> O	31	carbonate	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
3	carbide	Al <sub>4</sub> C <sub>3</sub>	32	bicarbonat	(NH <sub>4</sub> )HCO <sub>3</sub>
4	chloride	Al <sub>2</sub> Cl <sub>3</sub>	33	perchlorate	NH <sub>4</sub> ClO <sub>4</sub>
5	chloride hexahydrate	AlCl <sub>3</sub> ·6H <sub>2</sub> O	34	chloride	NH <sub>4</sub> Cl
6	sodium chloride	AlNaCl <sub>4</sub>	35	chromate	(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>
7	fluoride	AlF <sub>3</sub> ·3½H <sub>2</sub> O	36	bichromate	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
8	fluosilicate	Al <sub>2</sub> (SiF <sub>6</sub> ) <sub>3</sub>	37	citrate	(NH <sub>4</sub> ) <sub>2</sub> HC <sub>6</sub> H <sub>5</sub> O <sub>7</sub>
9	iodide	AlI <sub>3</sub>	38	fluoride	NH <sub>4</sub> F
10	nitrate nonahydrate	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	39	borofluoride	NH <sub>4</sub> BF <sub>4</sub>
11	oxide	α-Al <sub>2</sub> O <sub>3</sub>	40	fluosilicate	(NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub>
12	Diaspore	AlHO <sub>2</sub>	41	formate	HCOONH <sub>4</sub>
13	Bauxite	Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O	42	iodide	NH <sub>4</sub> I
14	β-Alumina	Na <sub>2</sub> O·11Al <sub>2</sub> O <sub>3</sub>	43	paramolybdate	(NH <sub>4</sub> ) <sub>6</sub> ·Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O
15	Aluminum silicate (sillimanite)	Al <sub>2</sub> SiO <sub>5</sub>	44	phosphomolyhdate trihydrate	(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ·12MoO <sub>3</sub> ·3H <sub>2</sub> O
16	Muscovite (common mica)	H <sub>2</sub> KAl <sub>3</sub> (SiO <sub>4</sub> ) <sub>3</sub>	45	nitrate (orthorhombic)	NH <sub>4</sub> NO <sub>3</sub>
17	Kaolin	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	46	nitrite	NH <sub>4</sub> NO <sub>2</sub>
18	Bentonite		47	nitrosophenylhydroxylamine	C <sub>6</sub> H <sub>5</sub> N·NO·ONH <sub>4</sub>
19	Aluminum sulfate	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	48	oxalate monohydrate	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O
20	sulfate octadecahydrate	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	49	oxalate, acid	(NH <sub>4</sub> )HC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O
21	ammonium sulfate (alum)	AlNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	50	phenolsulfonate	C <sub>6</sub> H <sub>4</sub> (OH)SO <sub>3</sub> NH <sub>4</sub>
22	potassium sulfate (alum)	AlK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	51	monohydrogen phosphate	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>
23	sodium sulfate (alum)	AlNa(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	52	dihydrogen phosphate	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>
24	sulfide	Al <sub>2</sub> S <sub>3</sub>	53	hypophosphite	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>2</sub>
25	Ammonium acetate	CH <sub>3</sub> COONH <sub>4</sub>	54	picrate monohydrate	C <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub> ·ONH <sub>4</sub> ·H <sub>2</sub> O
26	arsenate trihydrate	(NH <sub>4</sub> ) <sub>2</sub> AsO <sub>4</sub> ·3H <sub>2</sub> O	55	salicylate	C <sub>6</sub> H <sub>4</sub> (OH)COONH <sub>4</sub>
27	benzoate	C <sub>6</sub> H <sub>5</sub> COONH <sub>4</sub>	56	succinate	(CH <sub>2</sub> COONH <sub>4</sub> ) <sub>2</sub>
28	horate		57	sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
29	bromide	NH <sub>4</sub> Br	58	persulfate	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>
			59	hydrogen sulfate	NH <sub>4</sub> HSO <sub>4</sub>

(Continued on succeeding pages)



TABLE XI. INDEX TO POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

Pattern No.	Name	Formula	Pattern No.	Name	Formula
60	Ammonium sulfite monohydrate	$(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$	155	Cadmium hydroxide	$\text{Cd}(\text{OH})_2$
61	tartrate	$(\text{CHOH})_2(\text{CO}_2\text{NH}_4)_2$	156	potassium iodide	$2\text{KI} \cdot \text{CdI}_2 \cdot 2\text{H}_2\text{O}$
62	thiocyanate	$\text{NH}_4\text{CNS}$	157	nitrate tetrahydrate	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
63	thiosulfate	$(\text{NH}_4)_2\text{S}_2\text{O}_3$	158	oxalate	$\text{CdC}_2\text{O}_4$
64	tungstate	$(\text{NH}_4)_2\text{WO}_4 \cdot n\text{H}_2\text{O}$	159	oxalate trihydrate	$\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$
65	phosphotungstate	$3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 6\text{WO}_3 \cdot 9\text{H}_2\text{O}$	160	oxide	$\text{CdO}$
66	metavanadate	$\text{NH}_4\text{VO}_3$	161	ferrite	$\text{CdFe}_2\text{O}_4$
			162	phosphate	$\text{Cd}_3(\text{PO}_4)_2$
			163	salicylate	$\text{Cd}(\text{C}_6\text{H}_4\text{OHCOO})_2 \cdot \text{H}_2\text{O}$
			164	sulfate	$3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$
			165	tungstate	$\text{CdWO}_4$
67	Antimony	Sb	166	Calcium metal	Ca
68	arsenate	$\text{SbAsO}_4$	167	acetate	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$
69	arsenite		168	acetate monohydrate	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$
70	tribromide	$\text{SbBr}_3$	169	aluminum alloy (22% Ca)	
71	trichloride	$\text{SbCl}_3$	170	Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$
72	oxychloride	$\text{SbOCl}$	171	Pentacalcium aluminate	$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$
73	trifluoride	$\text{SbF}_3$	172	Calcium arsenate	$\text{Ca}_3(\text{AsO}_4)_2$
74	triiodide	$\text{SbI}_3$	173	arsenite	$\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$
75	trioxide	$\text{Sb}_2\text{O}_3$	174	benzoate	
76	pentoxide	$\text{Sb}_2\text{O}_5$	175	borate	$\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
77	potassium sulfurated	$\text{K}_2\text{S} \cdot \text{Sb}_2\text{S}_3$	176	bromide	$\text{CaC}_2 \text{ I}$
78	sulfate	$\text{Sb}_2(\text{SO}_4)_3$	177	carbide (tetragonal)	$\text{CaC}_2 \text{ II}$
79	trisulfide (stibnite)	$\text{Sb}_2\text{S}_3$	178	carbide II	$\text{CaC}_2 \text{ III}$
80	tartrate	$\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 6\text{H}_2\text{O}$	179	carbide III	$\text{CaCO}_3$
81	Antimonyl potassium tartrate	$(\text{SbO})\text{KC}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$	180	carbonate (calcite)	$\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$
			181	chlorate	$\text{CaCl}_2$
82	Arsenic metal	As	182	chloride	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$
83	iodide (ous)	$\text{AsI}_3$	183	chloride monohydrate	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
84	trioxide (ous)	$\text{As}_2\text{O}_3$	184	chloride dihydrate	$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$
85	pentoxide	$\text{As}_2\text{O}_5$	185	chloride tetrahydrate	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
86	trisulfide (ous), (orpiment)	$\text{As}_2\text{S}_3$	186	chloride hexahydrate	$\text{CaCl}_2 \cdot \text{CaF}_2$
			187	chlorofluoride	$\text{Ca}(\text{ClO})_2 \cdot 4\text{H}_2\text{O}$
87	Barium metal	Ba	188	bypochlorite	$\text{CaCrO}_4$
88	acetate monohydrate	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	189	chromate	$\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$
89	borate		190	chromate dihydrate	$\text{CaCr}_2\text{O}_7$
90	carbonate	$\text{BaCO}_3$	191	dichromate	$\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$
91	chlorate	$\text{Ba}(\text{ClO}_3)_2$	192	citrate	$\text{CaCN}_2$
92	chlorate monohydrate	$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	193	cyanamide	$\text{Ca}(\text{CN})_2$
93	perchlorate trihydrate	$\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	194	cyanide	$\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$
94	chloride	$\text{BaCl}_2$	195	ferrocyanide	$\text{CaK}_2\text{Fe}(\text{CN})_6$
95	chloride dihydrate	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	196	potassium ferrocyanide	$\text{CaF}_2$
96	chromate	$\text{BaCrO}_4$	197	fluoride	$\text{CaSiF}_6$
97	citrate	$\text{Ba}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 7\text{H}_2\text{O}$	198	fluosilicate	$\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$
98	cyanide	$\text{Ba}(\text{CN})_2$	199	fluosilicate dihydrate	$\text{Ca}(\text{HCO}_2)_2$
99	fluoride	$\text{BaF}_2$	200	formate	$\text{Ca}(\text{CH}_2\text{OHCOO})_2$
100	titanium fluoride	$\text{BaTiF}_6$	201	glycolate	$\text{Ca}(\text{CH}_2\text{OHCOO})_2 \cdot 3\text{H}_2\text{O}$
101	fluosilicate	$\text{BaSiF}_6$	202	glycolate trihydrate	$\text{Ca}(\text{CH}_2\text{OHCOO})_2 \cdot 3\text{H}_2\text{O}$
102	formate	$\text{Ba}(\text{HCO}_2)_2$	203	glycolate hydrate	$\text{Ca}(\text{CH}_2\text{OHCOO})_2 \cdot 3\text{H}_2\text{O}$
103	hydroxide octahydrate	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	204	hippurate	
104	iodate	$\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	205	hydride	$\text{CaH}_2$
105	manganate	$\text{BaMnO}_4$	206	hydroxide	$\text{Ca}(\text{OH})_2$
106	permanganate	$\text{Ba}(\text{MnO}_4)_2$	207	iodate	$\text{Ca}(\text{IO}_3)_2$
107	nitrate	$\text{Ba}(\text{NO}_3)_2$	208	iodide	$\text{CaI}_2 \cdot 4\text{H}_2\text{O}$
108	nitrite monohydrate	$\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$	209	permanganate	$\text{Ca}(\text{MnO}_4)_2 \cdot 4\text{H}_2\text{O}$
109	oxalate	$\text{BaC}_2\text{O}_4$	210	nitrate	$\text{Ca}(\text{NO}_3)_2$
110	oxide	$\text{BaO}$	211	nitrate tetrahydrate	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
111	peroxide	$\text{BaO}_2$	212	nitrite	$\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$
112	phenolsulfonate	$\text{Ba}(\text{C}_6\text{H}_4\text{OH} \cdot \text{SO}_3)_2$	213	oxalate	$\text{CaC}_2\text{O}_4$
113	phosphate	$\text{Ba}_3(\text{PO}_4)_2$	214	oxide	$\text{CaO}$
114	phosphite		215	peroxide	$\text{CaO}_2$
115	hypophosphite	$\text{Ba}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$	216	phenolsulfonate	$(\text{C}_6\text{H}_4\text{OHSO}_3)_2\text{Ca} \cdot \text{H}_2\text{O}$
116	sulfate	$\text{BaSO}_4$	217	hydrogen phosphite	$\text{CaHPO}_4$
117	sulfide	$\text{BaS}$	218	hydrogen phosphate dihydrate	$\text{CaH}_2\text{P}_2\text{O}_7$
118	sulfite	$\text{BaSO}_3$	219	dihydrogen phosphite	$\text{CaH}_2\text{P}_2\text{O}_7$
119	tartrate	$\text{BaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$	220	dihydrogen phosphate monohydrate	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
120	thiocyanate	$\text{Ba}(\text{CNS})_2 \cdot 2\text{H}_2\text{O}$	221	orthophosphate	$\text{Ca}_3(\text{PO}_4)_2$
121	thiosulfate monohydrate	$\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$	222	orthophosphate monohydrate	$\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
122	borotungstate		223	chlorohydrophosphate	
123	valerianate	$\text{Ba}(\text{C}_4\text{H}_9\text{CO}_2)_2$	224	glycerophosphate	$\text{CaO}_2 \cdot \text{PO} \cdot \text{OC}_3\text{H}_5(\text{OH})_2$
			225	lactophosphate	
124	Beryllium metal	Be	226	pyrophosphate	$\text{Ca}_2\text{P}_2\text{O}_7$
125	oxide	$\text{BeO}$	227	phosphide	$\text{Ca}_3\text{P}_2$
126	sulfate	$\text{BeSO}_4$	228	hyp phosphite	$\text{Ca}(\text{H}_2\text{PO}_2)_2$
127	sulfate tetrahydrate	$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$	229	sodium hypophosphite	$\text{Ca}(\text{NaH}_2\text{PO}_2)_2$
			230	salicylate	$\text{Ca}(\text{C}_6\text{H}_4\text{OHCOO})_2 \cdot 3\text{H}_2\text{O}$
128	Bismuth metal	Bi	231	silicate	$\text{CaSiO}_3$
129	acetate	$\text{Bi}(\text{C}_2\text{H}_3\text{O}_2)_3$	232	Dicalcium silicate (low)	$\alpha\text{-Ca}_2\text{SiO}_4$
130	benzoate	$\text{Bi}(\text{C}_6\text{H}_5\text{COO})_3$	233	Dicalcium silicate (high)	$\beta\text{-Ca}_2\text{SiO}_4$
131	oxybromide	$\text{BiOBr}$	234	Tricalcium silicate	$\text{Ca}_3\text{SiO}_5$
132	subcarbonate	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$	235	Calcium silicide	$\text{CaSi}_2$
133	oxychloride	$\text{BiOCl}$	236	sulfate	$\text{CaSO}_4$
134	chromate	$(\text{BiO})_2\text{CrO}_4$	237	sulfate hemihydrate	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
135	ammonium citrate		238	sulfate dihydrate (gypsum)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
136	hydroxide	$\text{Bi}(\text{OH})_3$	239	sulfide	$\text{CaS}$
137	lactate	$\text{Bi}(\text{C}_3\text{H}_5\text{O}_2)_3 \cdot 7\text{H}_2\text{O}$	240	sulfite	$\text{CaSO}_3$
138	$\beta$ -naphthol	$\text{BiO}_2 \cdot \text{C}_{10}\text{H}_7$	241	tartrate	$\text{CaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$
139	subnitrate	$\text{BiO} \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$	242	thiocyanate	$\text{Ca}(\text{CNS})_2 \cdot 3\text{H}_2\text{O}$
140	osmate		243	tungstate	$\text{CaWO}_4$
141	oxalate	$\text{Bi}_2(\text{C}_2\text{O}_4)_3$	244	urate	$\text{CaC}_5\text{H}_2\text{O}_3\text{N}_4$
142	trioxide (yellow)	$\text{Bi}_2\text{O}_3$			
143	tetraoxide	$\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	245	Carbon (graphite)	C
144	phosphate	$\text{BiPO}_4$	246	Acetaldehyde ammonia	$\text{CH}_3\text{CH}(\text{NH}_2)\text{OH}$
145	salicylate	$\text{Bi}_2(\text{C}_6\text{H}_4\text{OHCOO})_3$	247	Acetamide	$\text{CH}_3\text{CONH}_2$
146	sulfate	$\text{Bi}_2(\text{SO}_4)_3$	248	Acetanilide	$\text{CH}_3\text{CONHC}_6\text{H}_5$
			249	Acetophenetidin (pbenacetin)	$\text{C}_6\text{H}_4(\text{OC}_2\text{H}_5)(\text{NH} \cdot \text{CH}_2\text{CO})$ ; 1:4
147	Boric acid	$\text{H}_3\text{BO}_3$	250	Antipyrine (1-phenyl-2,3-dimethyl pyrazolone)	$\text{C}_{11}\text{H}_{12}\text{ON}_2$
148	Boron carbide	$\text{B}_4\text{C}$	251	Aspirin (acetylsalicylic acid)	$\text{C}_9\text{H}_8\text{O}_4 \cdot \text{HCO}_2\text{CH}_3$
			252	Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$
149	Cadmium metal	Cd	253	Benzophenone	$(\text{C}_6\text{H}_5)_2\text{CO}$
150	acetate	$\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	254	<i>o</i> -Chlorobenzoic acid	$\text{C}_6\text{H}_4\text{ClCOOH}$
151	bromate	$\text{Cd}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$	255	$\beta$ -Chloronaphthalene	$\text{C}_{10}\text{H}_7\text{Cl}$
152	carbonate	$\text{CdCO}_3$	256	<i>p</i> -Chloro- <i>o</i> -nitroaniline	$\text{C}_6\text{H}_3\text{ClNO}_2 \cdot \text{NH}_2$
153	chloride	$\text{CdCl}_2$	257	Cinnamic acid	$\text{C}_6\text{H}_5\text{CH} \cdot \text{CHCOOH}$
154	chloride, hydrated	$\text{CdCl}_2 \cdot 2 1/2\text{H}_2\text{O}$	258	Citric acid	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$



TABLE XI. INDEX TO POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

Pattern No.	Name	Formula	Pattern No.	Name	Formula
259	Coumarin	C <sub>9</sub> H <sub>6</sub> O <sub>2</sub>	354	Copper ammonium chloride (ic)	CuCl <sub>2</sub> ·2NH <sub>4</sub> Cl·2H <sub>2</sub> O
260	2,6-Dibromo-4-nitrophenol	NO <sub>2</sub> C <sub>6</sub> H <sub>2</sub> Br <sub>2</sub> OH	355	potassium chloride (ic)	CuCl <sub>2</sub> ·2KCl·2H <sub>2</sub> O
261	<i>p</i> -Dichlorobenzene	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	356	chromate (ic)	CuCrO <sub>4</sub> ·2CuO·2H <sub>2</sub> O
262	2,5-Dichlorobenzophenone	(C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> ) <sub>2</sub> CO	357	ammonium chromate (ic)	
263	Diphenylene oxide	(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> O	358	dichromate (ic)	CuCr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O
264	Diphenyl sulfoxide	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO	359	citrate (ic)	2Cu <sub>2</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·5H <sub>2</sub> O
265	Diphenyl urea	(C <sub>6</sub> H <sub>5</sub> NH) <sub>2</sub> CO	360	cyanide (ous)	CuCN
266	Ethyl amine hydrochloride	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> Cl	361	potassium cyanide (ous)	CuK <sub>3</sub> (CN) <sub>4</sub>
267	Glycine	CH <sub>2</sub> NH <sub>2</sub> COOH	362	ferrocyanide (ic)	Cu <sub>2</sub> Fe(CN) <sub>6</sub> ·7H <sub>2</sub> O
268	Glycollic acid	CH <sub>2</sub> OHCOOH	363	potassium ferrocyanide (ic)	K <sub>2</sub> CuFe(CN) <sub>6</sub>
269	Hexamethylenetetramine	(CH <sub>2</sub> ) <sub>6</sub> N <sub>4</sub>	364	fluoride dihydrate (ic)	CuF <sub>2</sub> ·2H <sub>2</sub> O
270	Imino diacetic acid	NH(CH <sub>2</sub> COOH) <sub>2</sub>	365	ammonium fluoride	(NH <sub>4</sub> ) <sub>2</sub> CuF <sub>4</sub> ·2H <sub>2</sub> O
271	Iodoacetylene	C <sub>2</sub> I <sub>2</sub>	366	formate (ic)	Cu(CHO <sub>2</sub> ) <sub>2</sub>
272	<i>o</i> -Iodophenol	C <sub>6</sub> H <sub>4</sub> IOH	367	iodide (ous)	CuI
273	Isatin	C <sub>6</sub> H <sub>3</sub> CO·COH:N	368	magnesium alloy	CuMg <sub>2</sub>
274	Lactose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ·H <sub>2</sub> O	369	magnesium alloy	Cu <sub>2</sub> Mg
275	Maleic acid	C <sub>2</sub> H <sub>2</sub> (COOH) <sub>2</sub>	370	nitrate (ic)	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O
276	Napbtbalene	C <sub>10</sub> H <sub>8</sub>	371	oxide (ous)	Cu <sub>2</sub> O
277	$\alpha$ -Naphthol	C <sub>10</sub> H <sub>7</sub> OH	372	oxide (ic), (tennorite)	CuO
278	2-Naphthol-6-sulfonic acid	C <sub>10</sub> H <sub>6</sub> OHSO <sub>3</sub> H	373	cobalt spinel	CuCo <sub>2</sub> O <sub>4</sub>
279	Nitrile triacetic acid	N(CH <sub>2</sub> COOH) <sub>3</sub>	374	phenol sulfonate	(C <sub>6</sub> H <sub>4</sub> OHHSO <sub>3</sub> ) <sub>2</sub> Cu·6H <sub>2</sub> O
280	<i>p</i> -Nitroaniline	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ·NH <sub>2</sub>	375	phosphate (fused), (ic)	
281	<i>m</i> -Nitrobenzaldehyde	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	376	phosphate (ic)	Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O
282	Oxalic acid dibydrate	(COOH) <sub>2</sub> ·2H <sub>2</sub> O	377	phosphate (ic), (libethenite)	CuOH·CuPO <sub>4</sub>
283	Pentachlorobenzene	C <sub>6</sub> HCl <sub>5</sub>	378	salicylate (ic)	Cu(C <sub>6</sub> H <sub>4</sub> OHCOO) <sub>2</sub> ·4H <sub>2</sub> O
284	<i>o</i> -C-Phenylphenol	<i>o</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> OH	379	sulfate (ic)	CuSO <sub>4</sub>
285	<i>p</i> -Phenylphenol	<i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> OH	380	sulfate (ic) monohydrate	CuSO <sub>4</sub> ·H <sub>2</sub> O
286	Salicylic acid	C <sub>6</sub> H <sub>4</sub> OHCOOH	381	sulfate (ic) pentahydrate	CuSO <sub>4</sub> ·5H <sub>2</sub> O
287	Sucrose (sugar)	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	382	ammonium sulfate (ic)	CuSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O
288	Sulfonal (acetone diethyl sulfone)	(CH <sub>3</sub> ) <sub>2</sub> C(SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	383	potassium sulfate (ic)	CuSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O
289	Tartaric acid ( <i>dl</i> )	C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> ·H <sub>2</sub> O	384	Chalcopyrite	CuFeS <sub>2</sub>
290	Tetrabromobenzene	C <sub>6</sub> H <sub>2</sub> Br <sub>4</sub> ·(1,2,4,5)	385	Copper sulfite (ous)	Cu <sub>2</sub> SO <sub>3</sub> ·H <sub>2</sub> O
291	<i>p</i> -Toluene sulfonylamide	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NH <sub>2</sub>	386	tartrate (ic)	CuC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·3H <sub>2</sub> O
292	Triclorobenzyl cyanide	C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> ·CH <sub>2</sub> CN	387	thiocyanate (ous)	CuCNS
293	Trional (methyl ethyl ketone diethyl sulfone)	C <sub>2</sub> H <sub>5</sub> CH <sub>3</sub> C:(SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>			
294	Urea	NH <sub>2</sub> ·CO·NH <sub>2</sub>	388	Erbium chloride	ErCl <sub>3</sub> ·6H <sub>2</sub> O
			389	oxide	Er <sub>2</sub> O <sub>3</sub>
295	Cerium metal (commercial)	Ce	390	Germanium dioxide	GeO <sub>2</sub>
296	chloride	CeCl <sub>3</sub>			
297	nitrate	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O			
298	oxalate	Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	391	Gold metal	Au
299	oxide (ic)	CeO <sub>2</sub>	392	cyanide (ous)	AuCN
300	sulfate (ic)	Ce(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	393	potassium cyanide (ous)	AuK(CN) <sub>2</sub>
301	sulfate (ous)	Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>			
302	Cesium aluminum sulfate (alum)	CsAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	394	Indium metal	In
303	chloride	CsCl	395	trichloride	InCl <sub>3</sub>
304	rubidium chloride	CsCl·RbCl	396	oxide	In <sub>2</sub> O <sub>3</sub>
305	iodide	CsI			
306	dicloroiodide	CsICl <sub>2</sub>	397	Iodine	I <sub>2</sub>
307	nitrate	CsNO <sub>3</sub>	398	pentoxide	I <sub>2</sub> O <sub>5</sub>
308	sulfate	Cs <sub>2</sub> SO <sub>4</sub>			
309	Chromium metal	Cr	399	Iridium metal	Ir
310	borate		400	trichloride	IrCl <sub>3</sub>
311	bromide	CrBr <sub>3</sub> ·6H <sub>2</sub> O			
312	fluoride tetrahydrate	CrF <sub>3</sub> ·4H <sub>2</sub> O	401	Iron	Fe
313	nitrate	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	402	aluminum alloy I	FeAl
314	oxalate	Cr <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	403	aluminum alloy II	FeAl <sub>3</sub>
315	oxide (ic)	Cr <sub>2</sub> O <sub>3</sub>	404	aluminum alloy III	Fe <sub>2</sub> Al <sub>5</sub>
316	trioxide (ic)	CrO <sub>3</sub>	405	arsenate (ous)	Fe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
317	ammonium sulfate (partly dehydrated)	Cr(NH <sub>4</sub> )(SO <sub>4</sub> ) <sub>2</sub> ·<12H <sub>2</sub> O	406	cacodylate (ic)	Fe[(CH <sub>3</sub> ) <sub>2</sub> AsO <sub>2</sub> ] <sub>3</sub>
318	ammonium sulfate (alum)	Cr(NH <sub>4</sub> )(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	407	chloride (ic)	FeCl <sub>3</sub>
319	potassium sulfate (alum)	CrK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	408	chloride (ic) hexahydrate	FeCl <sub>3</sub> ·6H <sub>2</sub> O
			409	chloride (ous) dihydrate	FeCl <sub>2</sub> ·2H <sub>2</sub> O
			410	chloride (ous) tetrahydrate	FeCl <sub>2</sub> ·4H <sub>2</sub> O
			411	ammonium chloride	
			412	ferrocyanide (ic), (Prussian blue)	Fe <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub>
320	Cobalt metal	Co	413	fluoride (ic)	FeF <sub>3</sub> ·4 <sup>1</sup> / <sub>2</sub> H <sub>2</sub> O
321	acetate (ous)	Co(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	414	formate (ic)	Fe(HCO <sub>2</sub> ) <sub>3</sub> ·H <sub>2</sub> O
322	arsenate (ous)	Co <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	415	lactate (ous)	Fe(C <sub>3</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O
323	bromide (ous)	CoBr <sub>2</sub>	416	nitrate (ic)	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O
324	carbonate (ous)	CoCO <sub>3</sub>	417	nitride I	Fe <sub>3</sub> N
325	chloride (ous)		418	nitride II	Fe <sub>4</sub> N
326	chloride hexahydrate (ous)	CoCl <sub>2</sub> ·6H <sub>2</sub> O	419	oxalate (ous)	FeC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O
327	chloride (luteo)	Co(NH <sub>3</sub> ) <sub>6</sub> Cl <sub>3</sub>	420	ammonium oxalate (ic)	(NH <sub>4</sub> ) <sub>3</sub> Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>
328	chloride (purpureo)	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sub>3</sub>	421	potassium oxalate (ic)	K <sub>2</sub> Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
329	chromate (ous)	CoCrO <sub>4</sub>	422	sodium oxalate (ic)	2Na <sub>3</sub> Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O
330	bydroxide (ous)	Co(OH) <sub>2</sub>	423	oxide (ic)	Fe <sub>2</sub> O <sub>3</sub>
331	manganese spinel	(Mn,Co)(Mn,Co) <sub>2</sub> O <sub>4</sub> ·2Co:Mn	424	Goethite	FeHO <sub>2</sub>
332	nitrate hexahydrate	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	425	Iron oxide (ous)	FeO
333	oxalate (ous)	CoC <sub>2</sub> O <sub>4</sub>	426	ferrite (magnetite)	Fe <sub>3</sub> O <sub>4</sub>
334	oxide (ous)	CoO	427	chrome-aluminate	FeO(Cr <sub>2</sub> O <sub>3</sub> ·Al <sub>2</sub> O <sub>3</sub> )
335	oxide (ous), (ic)	CoCo <sub>2</sub> O <sub>4</sub>	428	phenolsulfonate (ous)	(C <sub>6</sub> H <sub>4</sub> OHHSO <sub>3</sub> ) <sub>2</sub> ·Fe
336	phospbate (ous)	Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	429	phosphide	Fe <sub>2</sub> P
337	stannate (ous)		430	hypophosphite (ic)	Fe(H <sub>2</sub> PO <sub>2</sub> ) <sub>3</sub>
338	sulfate (ous)	CoSO <sub>4</sub>	431	salicylate (ic)	
339	ammonium sulfate (ous)	CoSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	432	silicide	FeSi
			433	disilicide	FeSi <sub>2</sub>
340	Columbium metal	Cb	434	sulfate (ic)	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O
			435	sulfate (ous)	FeSO <sub>4</sub>
341	Copper metal	Cu	436	sulfate monohydrate (ous)	FeSO <sub>4</sub> ·H <sub>2</sub> O
342	acetoarsenite (ic), (Paris green)	(CuOAs <sub>2</sub> O <sub>3</sub> ) <sub>3</sub> Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	437	sulfate trihydrate (ous)	FeSO <sub>4</sub> ·3H <sub>2</sub> O
343	aluminate	CuAl <sub>2</sub> O <sub>4</sub>	438	sulfate beptahydrate (ous)	FeSO <sub>4</sub> ·7H <sub>2</sub> O
344	benzoate (ic)	Cu(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O	439	ammonium sulfate (partly dehydrated), (ic)	FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·<12H <sub>2</sub> O
345	beryllium alloy (12% Be)		440	ammonium sulfate (ic), (alum)	FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O
346	borate (ic)		441	ammonium sulfate (ous)	FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O
347	bromide (ous)	CuBr	442	sulfide (ous)	FeS
348	bromide (ic)	CuBr <sub>2</sub>	443	disulfide (pyrite)	FeS <sub>2</sub>
349	carbonate (ic), (azurite)	2CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	444	tartrate (ous)	FeC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>
350	carbonate (ic), (malachite)	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>			
351	chloride (ous)	CuCl	445	Lead metal	Pb
352	chloride (ic)	CuCl <sub>2</sub>	446	acetate	Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·3H <sub>2</sub> O
353	chloride (ic) dihydrate	CuCl <sub>2</sub> ·2H <sub>2</sub> O	447	acetate (basic)	Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> Pb(OH) <sub>2</sub> ·H <sub>2</sub> O



TABLE XI. INDEX TO POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

Pattern No.	Name	Formula	Pattern No.	Name	Formula
448	Lead antimoniate	$\text{Pb}_3(\text{SbO}_4)_2$	551	Magnesium urate	$\text{MgC}_5\text{H}_2\text{N}_4\text{O}_8$
449	hydrogen orthoarsenate	$\text{PbHAsO}_4$	552	vanadate	
450	bromide	$\text{PbBr}_2$			
451	carbonate	$\text{PbCO}_3$	553	Manganese ( $\alpha$ )	$\alpha\text{-Mn}$
452	carbonate (basic)	$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	554	( $\beta$ )	$\beta\text{-Mn}$
453	chloride	$\text{PbCl}_2$	555	acetate	$\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$
454	chromate	$\text{PbCrO}_4$	556	aluminate	$\text{MnAl}_2\text{O}_4$
455	ferrocyanide	$\text{Pb}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	557	benzoate	$\text{Mn}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$
456	fluoride (cubic)	$\text{PbF}_2$	558	borate	
457	fluosilicate	$\text{PbSiF}_6 \cdot 2\text{H}_2\text{O}$	559	carbonate	$\text{MnCO}_3$
458	formate	$\text{Pb}(\text{HCO}_2)_2$	560	chloride	$\text{MnCl}_2$
459	iodide	$\text{PbI}_2$	561	chloride monohydrate	$\text{MnCl}_2 \cdot \text{H}_2\text{O}$
460	nitrate	$\text{Pb}(\text{NO}_3)_2$	562	chloride dihydrate	$\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$
461	oxalate	$\text{PbC}_2\text{O}_4$	563	chloride tetrahydrate	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$
462	oxide (litharge)	$\text{PbO}$	564	fluoride	$\text{MnF}_2$
463	dioxide	$\text{PbO}_2$	565	oxalate	$\text{MnC}_2\text{O}_4$
464	oxide (minium)	$\text{Pb}_3\text{O}_4$	566	oxalate hydrate	$\text{MnC}_2\text{O}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$
465	phosphate	$\text{Pb}_3(\text{PO}_4)_2$	567	oxide	$\text{MnO}$
466	sulfate	$\text{PbSO}_4$	568	dioxide	$\text{MnO}_2$
467	sulfide	$\text{PbS}$	569	manganic oxide (ous)	$\text{Mn}_3\text{O}_4$
468	thiosulfate	$\text{PbS}_2\text{O}_3$	570	cohalt spinel	$(\text{Mn}, \text{Co}) (\text{Mn}, \text{Co})_2\text{O}_4; 2\text{Mn}:\text{Co}$
			571	phosphate	$\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$
469	Lithium metal	$\text{Li}$	572	hypophosphite	$\text{Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$
470	benzoate	$\text{Li}(\text{C}_6\text{H}_5\text{COO})$	573	ammonium sulfate	$\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
471	borate	$\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	574	sulfate tetrahydrate	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$
472	bromide	$\text{LiBr}$	575	sulfide	$\text{MnS}$
473	bromide dihydrate	$\text{LiBr} \cdot 2\text{H}_2\text{O}$	576	tartrate	$\text{MnC}_4\text{H}_4\text{O}_6$
474	carbonate	$\text{Li}_2\text{CO}_3$			
475	chloride	$\text{LiCl}$	577	Mercury acetate (ic)	$\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$
476	chloride monohydrate	$\text{LiCl} \cdot \text{H}_2\text{O}$	578	acetate (ous)	$(\text{HgC}_2\text{H}_3\text{O}_2)_2$
477	chromate	$\text{Li}_2\text{CrO}_4$	579	benzoate (ic)	$\text{Hg}(\text{C}_6\text{H}_5\text{COO})_2$
478	chromate dihydrate	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$	580	bromide (ic)	$\text{HgBr}_2$
479	dichromate	$\text{Li}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	581	bromide (ous)	$\text{Hg}_2\text{Br}_2$
480	fluoride	$\text{LiF}$	582	perchlorate (ic)	$\text{Hg}(\text{ClO}_4)_2$
481	hydroxide	$\text{LiOH}$	583	chloride (ic)	$\text{HgCl}_2$
482	iodide	$\text{LiI}$	584	chloride (ous)	$\text{Hg}_2\text{Cl}_2$
483	iodide trihydrate	$\text{LiI} \cdot 3\text{H}_2\text{O}$	585	ammonium chloride	$\text{HgCl}_2 \cdot 3\text{HgO}$
484	lactate	$\text{LiC}_3\text{H}_5\text{O}_3$	586	oxychloride (ic)	$\text{HgCrO}_4$
485	nitrate	$\text{LiNO}_3$	587	chromate (ic)	$\text{Hg}_2\text{CrO}_4$
486	oxalate	$\text{Li}_2\text{C}_2\text{O}_4$	588	chromate (ous)	$\text{Hg}(\text{CN})_2$
487	salicylate	$\text{LiC}_6\text{H}_4\text{OH} \cdot \text{COO}$	589	cyanide (ic)	$\text{HgI}_2$
488	sulfate	$\text{Li}_2\text{SO}_4$	590	iodide (ic)	$\text{Hg}_2\text{I}_2$
489	sulfate monohydrate	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	591	iodide (ous)	$\text{K}_2\text{HgI}_4 \cdot 3\text{H}_2\text{O}$
490	tartrate	$\text{Li}_2\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$	592	potassium iodide (ic)	$\text{HgNO}_3 \cdot \text{H}_2\text{O}$
491	acid tartrate	$\text{LiHC}_4\text{H}_4\text{O}_6$	593	nitrate (ous)	$\text{HgC}_2\text{O}_4$
			594	oxalate (ic)	$\text{HgO}$
492	Magnesium metal	$\text{Mg}$	595	oxide (ic), (orthorhombic)	$\text{Hg}_3(\text{PO}_4)_2$
493	acetate	$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$	596	phosphate (ic)	$\text{Hg}_3\text{PO}_4$
494	acetate tetrahydrate	$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	597	phosphate (ous)	$\text{Hg}(\text{CH}_2\text{COO})_2$
495	aluminum alloy I	$\text{Mg}_2\text{Al}_3$	598	succinate (ic)	$\text{HgSO}_4$
496	aluminum alloy II	$\text{Mg}_3\text{Al}_2$	599	sulfate (ic)	$\text{HgSO}_4 \cdot 2\text{HgO}$
497	aluminate	$\text{MgAl}_2\text{O}_4$	600	sulfate (basic)	$\text{Hg}_2\text{SO}_4$
498	arsenate	$2\text{MgHAsO}_4 \cdot 13\text{H}_2\text{O}$	601	sulfate (ous)	$\text{HgS}$
499	benzoate	$\text{Mg}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$	602	sulfide (black)	$\text{HgS}$
500	borate		603	sulfide (red), (cinnabar)	$\text{HgS}$
501	bromide hexahydrate	$\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$	604	sulfide thiocyanate (ous)	$\text{HgCNS}$
502	calcium alloy	$\text{Mg}_2\text{Ca}$			
503	carbide	$\text{Mg}_2\text{C}_3$	605	Molybdenum metal	$\text{Mo}$
504	carbonate trihydrate (nesquehonite)	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	606	acid (ic)	$\text{H}_2\text{MoO}_4$
505	carbonate (hydromagnesite)	$5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$	607	carbide	$\text{Mo}_2\text{C}$
506	Dolomite	$\text{MgCO}_3 \cdot \text{CaCO}_3$	608	oxalate	
507	Magnesium perchlorate	$\text{Mg}(\text{ClO}_4)_2$	609	oxide (ic)	$\text{MoO}_3$
508	perchlorate trihydrate	$\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	610	sesquioxide	$\text{Mo}_2\text{O}_3$
509	perchlorate hexahydrate	$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	611	silicide	$\text{MoSi}_2$
510	chloride	$\text{MgCl}_2$			
511	chloride hexahydrate	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	612	Neodymium chloride	$\text{NdCl}_3$
512	ammonium chloride	$\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$	613	chloride hexahydrate	$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$
513	chromate	$\text{MgCrO}_4 \cdot 7\text{H}_2\text{O}$	614	ammonium nitrate	
514	citrate	$\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 14\text{H}_2\text{O}$			
515	fluoride	$\text{MgF}_2$	615	Nickel metal	$\text{Ni}$
516	fluosilicate	$\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$	616	acetate	$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$
517	formate	$\text{Mg}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$	617	aluminate	$\text{NiAl}_2\text{O}_4$
518	hydroxide	$\text{Mg}(\text{OH})_2$	618	chloride	$\text{NiCl}_2$
519	iodide	$\text{MgI}_2 \cdot 8\text{H}_2\text{O}$	619	chloride dihydrate	$\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$
520	lactate	$\text{Mg}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$	620	chloride tetrahydrate	$\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$
521	lead alloy	$\text{Mg}_2\text{Pb}$	621	chloride hexahydrate	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
522	mercury alloy	$\text{Mg}_3\text{Hg}$	622	cyanide	$\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$
523	nitrate	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	623	fluoride	$\text{Ni}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$
524	nitride	$\text{Mg}_3\text{N}_2$	624	formate	$\text{Ni}(\text{OH})_2$
525	oxalate	$\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	625	hydroxide	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
526	oxide	$\text{MgO}$	626	nitrate	$\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
527	ferrite	$\text{MgFe}_2\text{O}_4$	627	oxalate	$\text{NiO}$
528	phenolsulfonate	$(\text{C}_6\text{H}_4\text{OHSO}_3)_2\text{Mg}$	628	oxide	$\text{NiMn}_2\text{O}_4$
529	phosphate monohydrate	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	629	manganese spinel	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
530	phosphate dihydrate	$\text{Mg}(\text{H}_2\text{PO}_4)_2$	630	sulfate hexahydrate	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
531	phosphate tetrahydrate	$\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	631	sulfate heptahydrate	$\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
532	phosphate octahydrate	$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	632	ammonium sulfate	
533	ammonium phosphate	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	633	tartrate (ous)	
534	pyrophosphate	$\text{Mg}_2\text{P}_2\text{O}_7$			
535	hypophosphite	$\text{Mg}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$	634	Osmium metal	$\text{Os}$
536	lactophosphate				
537	silicate	$\text{MgSiO}_3$	635	Palladium metal	$\text{Pd}$
538	Dimagnesium silicate	$\text{Mg}_2\text{SiO}_4$	636	chloride	$\text{PdCl}_2$
539	Asbestos	$3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	637	nitrate	$\text{Pd}(\text{NO}_3)_2$
540	Magnesium silicide	$\text{Mg}_2\text{Si}$			
541	sulfate	$\text{MgSO}_4$	638	Phosphorus pentachloride	$\text{PCl}_5$
542	sulfate monohydrate	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	639	pentoxide	$\text{P}_2\text{O}_5$
543	sulfate hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	640	pentasulfide	$\text{P}_2\text{S}_5$
544	sulfate heptahydrate (Epsom salt)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	641	Phosphomolybdic acid	$20\text{MoO}_3 \cdot 2\text{H}_3\text{PO}_4 \cdot 48\text{H}_2\text{O}$
545	ethyl sulfate				
546	sulfide	$\text{MgS}$			
547	sulfite hexahydrate	$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$			
548	tartrate	$\text{MgC}_4\text{H}_4\text{O}_6 \cdot 5\text{H}_2\text{O}$			
549	thiosulfate	$\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$			
550	tin alloy	$\text{Mg}_2\text{Sn}$			



TABLE XI. INDEX TO POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

Pattern No.	Name	Formula	Pattern No.	Name	Formula
642	Platinum metal	Pt	740	Selenium (hexagonal)	Se
643	ammonium chloride (ic)	(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub>	741	Selenium acid (ous)	H <sub>2</sub> SeO <sub>3</sub>
644	potassium chloride (ic)	K <sub>2</sub> PtCl <sub>6</sub>			
645	potassium chloride (ous)	K <sub>2</sub> PtCl <sub>4</sub>			
646	sodium chloride		742	Silicon	Si
647	barium cyanide tetrahydrate	BaPt(CN) <sub>4</sub> ·4H <sub>2</sub> O	743	Silicon carbide (cubic)	SiC
648	magnesium cyanide		744	Carborundum commercial (cubic and hexagonal forms)	SiC
649	potassium cyanide	K <sub>2</sub> Pt(CN) <sub>4</sub> ·3H <sub>2</sub> O	745	Silicon dioxide (α-cristobalite)	SiO <sub>2</sub>
			746	dioxide (α-quartz)	SiO <sub>2</sub>
650	Potassium metal	K			
651	acetate	KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	747	Silver metal	Ag
652	arsenate		748	acetate	AgC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
653	arsenite		749	arsenate	Ag <sub>3</sub> AsO <sub>4</sub>
654	azide	KN <sub>3</sub>	750	bromate	AgBrO <sub>3</sub>
655	benzoate	K(C <sub>6</sub> H <sub>5</sub> COO)·3H <sub>2</sub> O	751	bromide	AgBr
656	tetraborate	K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O	752	carbonate	Ag <sub>2</sub> CO <sub>3</sub>
657	bromate	KBrO <sub>3</sub>	753	perchlorate	AgClO <sub>4</sub> ·H <sub>2</sub> O
658	bromide	KBr	754	chloride	AgCl
659	carbonate	K <sub>2</sub> CO <sub>3</sub>	755	chromate	Ag <sub>2</sub> CrO <sub>4</sub>
660	bicarbonate	KHCO <sub>3</sub>	756	citrate	Ag <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>
661	chlorate	KClO <sub>3</sub>	757	cyanide	AgCN
662	perchlorate	KClO <sub>4</sub>	758	potassium cyanide	
663	chloride	KCl	759	iodide (cubic)	AgI
664	chromate	K <sub>2</sub> CrO <sub>4</sub>	760	iodide (cubic and hexagonal)	AgI
665	dichromate	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	761	molybdate	Ag <sub>2</sub> MoO <sub>4</sub>
666	citrate	K <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·H <sub>2</sub> O	762	nitrate	AgNO <sub>3</sub>
667	cyanate	KCNO	763	nitrite	AgNO <sub>2</sub>
668	cyanide	KCN	764	oxide	Ag <sub>2</sub> O
669	ferricyanide	K <sub>3</sub> Fe(CN) <sub>6</sub>	765	phosphate	Ag <sub>3</sub> PO <sub>4</sub>
670	ferrocyanide	K <sub>4</sub> Fe(CN) <sub>6</sub>	766	sulfate	Ag <sub>2</sub> SO <sub>4</sub>
671	ferrocyanide trihydrate	K <sub>4</sub> Fe(CN) <sub>6</sub> ·3H <sub>2</sub> O	767	sulfide (orthorhombic)	Ag <sub>2</sub> S
672	fluoride	KF	768	tartrate	Ag <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>
673	fluoride dihydrate	KF·2H <sub>2</sub> O	769	vanadate	Ag <sub>4</sub> V <sub>2</sub> O <sub>7</sub>
674	fluosilicate	K <sub>2</sub> SiF <sub>6</sub>			
675	hydroxide	KOH	770	Sodium metal	Na
676	iodate	KIO <sub>3</sub>	771	acetate	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
677	iodate, acid	KIO <sub>3</sub> ·HIO <sub>3</sub>	772	acetate trihydrate	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ·3H <sub>2</sub> O
678	periodate	KIO <sub>4</sub>	773	uranyl zinc acetate	Na(UO <sub>2</sub> ) <sub>2</sub> Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> )
679	iodide	KI	774	amide	NaNH <sub>2</sub>
680	permanganate	KMnO <sub>4</sub>	775	arsenate	Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O
681	molybdate	K <sub>2</sub> MoO <sub>4</sub>	776	arsenate (methyl)	CH <sub>3</sub> AsO(ONa) <sub>2</sub> ·6H
682	nitrate	KNO <sub>3</sub>	777	arsenite	Na <sub>2</sub> HAsO <sub>3</sub>
683	nitrite	KNO <sub>2</sub>	778	asparaginate	
684	osmate	K <sub>2</sub> OsO <sub>4</sub> ·2H <sub>2</sub> O	779	azide	NaN <sub>3</sub>
685	oxalate	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	780	barbital	
686	oxalate monohydrate	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	781	hismuthate	NaBiO <sub>3</sub>
687	oxalate, acid	KHC <sub>2</sub> O <sub>4</sub> ·1/2H <sub>2</sub> O	782	tetraphorate	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O
688	phenolsulfonate	K(C <sub>6</sub> H <sub>4</sub> OHSO <sub>3</sub> )	783	tetraphorate decahydrate (borax)	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O
689	phenylate	C <sub>6</sub> H <sub>5</sub> OK	784	metaphorate	Na <sub>3</sub> (B <sub>3</sub> O <sub>6</sub> )
690	orthophosphate	K <sub>3</sub> PO <sub>4</sub>	785	perhorate	NaBO <sub>3</sub> ·2H <sub>2</sub> O
691	hydrogen phosphate	K <sub>2</sub> HPO <sub>4</sub>	786	borohenzoate	
692	hydrogen phosphate trihydrate	K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O	787	bromate	NaBrO <sub>3</sub>
693	dihydrogen phosphate	KH <sub>2</sub> PO <sub>4</sub>	788	bromide	NaBr
694	ammonium phosphate		789	butyrate	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COONa
695	pyrophosphate	K <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·3H <sub>2</sub> O	790	cacodylate	(CH <sub>3</sub> ) <sub>2</sub> AsO·ONa·3H <sub>2</sub> O
696	hypophosphite	KH <sub>2</sub> PO <sub>2</sub>	791	carbonate	Na <sub>2</sub> CO <sub>3</sub>
697	phthalimide	C <sub>8</sub> H <sub>4</sub> (CO) <sub>2</sub> NK	792	carbonate monohydrate	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
698	hydrogen phthalate	C <sub>8</sub> H <sub>4</sub> COOH·COOK	793	carbonate hydrate	Na <sub>2</sub> CO <sub>3</sub> ·2 1/2 H <sub>2</sub> O
699	salicylate	C <sub>6</sub> H <sub>4</sub> OHCOOK	794	carbonate decahydrate	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O
700	selenate	K <sub>2</sub> SeO <sub>4</sub>	795	hydrogen carbonate	NaHCO <sub>3</sub>
701	selenite	K <sub>2</sub> SeO <sub>3</sub>	796	potassium carbonate	Na <sub>2</sub> KCO <sub>3</sub>
702	selenocyanide	KSeCN	797	chlorate	NaClO <sub>3</sub>
703	Feldspar (microcline)	KAlSi <sub>3</sub> O <sub>8</sub>	798	perchlorate	NaClO <sub>4</sub>
704	Potassium sulfate	K <sub>2</sub> SO <sub>4</sub>	799	perchlorate monohydrate	NaClO <sub>4</sub> ·H <sub>2</sub> O
705	hydrogen sulfate	KHSO <sub>4</sub>	800	chloride	NaCl
706	persulfate	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	801	chromate	Na <sub>2</sub> CrO <sub>4</sub>
707	pyrosulfate	K <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	802	chromate tetrahydrate	Na <sub>2</sub> CrO <sub>4</sub> ·4H <sub>2</sub> O
708	ethyl sulfate	KC <sub>2</sub> H <sub>5</sub> SO <sub>4</sub>	803	dichromate dihydrate	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O
709	methyl sulfate	2KCH <sub>3</sub> SO <sub>4</sub> ·H <sub>2</sub> O	804	cinnamate	C <sub>6</sub> H <sub>5</sub> CH:CHCOONa
710	sulfite	K <sub>2</sub> SO <sub>3</sub> ·2H <sub>2</sub> O	805	citrate dihydrate	Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·2H <sub>2</sub> O
711	hydrogen sulfite	KHSO <sub>3</sub>	806	citrate hydrate	2Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·11H <sub>2</sub> O
712	pyrosulfite	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	807	cyanide	NaCN
713	benzene sulfonate	C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> K	808	ethylate	C <sub>2</sub> H <sub>5</sub> ONa
714	guaiacol sulfonate	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> K	809	ferrocyanide	Na <sub>4</sub> Fe(CN) <sub>6</sub>
715	indigo sulfonate		810	ferrocyanide decahydrate	Na <sub>4</sub> Fe(CN) <sub>6</sub> ·10H <sub>2</sub> O
716	toluene sulfonate		811	nitroferrocyanide	Na <sub>2</sub> Fe(CN) <sub>5</sub> NO·2H <sub>2</sub> O
717	tartrate	K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	812	fluoride	NaF
718	ammonium tartrate	K(NH <sub>4</sub> )C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	813	aluminum fluoride (cryolite)	Na <sub>3</sub> AlF <sub>6</sub>
719	hydrogen tartrate	KH(C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> )	814	fluosilicate	Na <sub>2</sub> SiF <sub>6</sub>
720	tellurite	K <sub>2</sub> TeO <sub>3</sub>	815	formate	NaHCO <sub>2</sub>
721	thiocarbonate	K <sub>2</sub> CS <sub>3</sub>	816	hippurate	
722	thiosulfate	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	817	hydroxide	NaOH
723	thiosulfate hydrate	3K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	818	iodate	NaIO <sub>3</sub>
724	thiocyanate	KCNS	819	periodate	Na <sub>2</sub> H <sub>3</sub> IO <sub>6</sub>
725	titanate	K <sub>2</sub> TiO <sub>3</sub>	820	iodide	NaI
726	tungstate	K <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	821	permanganate	NaMnO <sub>4</sub> ·3H <sub>2</sub> O
727	uranate	K <sub>2</sub> UO <sub>4</sub>	822	molybdate	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O
728	urate	KHC <sub>8</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	823	phosphomolybdate	
729	vanadate, meta	KVO <sub>3</sub>	824	naphthionate	
730	xanthogenate	KS <sub>2</sub> COC <sub>2</sub> H <sub>5</sub>	825	nitrate	NaNO <sub>3</sub>
			826	nitrate (cobaltic)	
731	Rhenium metal	Re	827	nitrite	NaNO <sub>2</sub>
			828	oxalate	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
732	Rhodium metal	Rh	829	hydrogen oxalate	NaHC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O
			830	peroxide	Na <sub>2</sub> O <sub>2</sub>
			831	p-phenolsulfonate	p-C <sub>6</sub> H <sub>4</sub> OHSO <sub>3</sub> Na·2H <sub>2</sub> O
733	Rubidium bromide	RbBr	832	nitrophenylate	
734	chloride	RbCl	833	dinitrophenylate	
735	iodide	RbI	834	orthophosphate	Na <sub>3</sub> PO <sub>4</sub>
736	nitrate	RhNO <sub>3</sub>	835	hydrogen phosphate	Na <sub>2</sub> HPO <sub>4</sub>
737	sulfate	Rh <sub>2</sub> SO <sub>4</sub>	836	hydrogen phosphate dihydrate	Na <sub>2</sub> HPO <sub>4</sub> ·2H <sub>2</sub> O
738	aluminum sulfate (alum)	RhAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	837	hydrogen phosphate dodecahydrate	Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O
			838	dihydrogen phosphate	NaH <sub>2</sub> PO <sub>4</sub>
739	Ruthenium metal	Ru	839	dihydrogen phosphate monohydrate	NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O



TABLE XI. INDEX TO POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Concluded)

Pattern No.	Name	Formula	Pattern No.	Name	Formula
840	Sodium hypophosphate	$\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$	921	Thorium nitrate	$\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$
841	metaphosphate	$\text{NaPO}_3$	922	oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2$
842	pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7$	923	dioxide	$\text{ThO}_2$
843	pyrophosphate decahydrate	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	924	sulfate	$\text{Th}(\text{SO}_4)_2$
844	ammonium hydrogen phosphate tetrahydrate	$\text{NaNH}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$	925	Tin metal	Sn
845	calcium glycerophosphate (duotonal)		926	antimony alloy	SnSb
846	phosphite	$\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$	927	chloride (ic)	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$
847	hypophosphite	$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	928	ammonium chloride (ic)	$(\text{NH}_4)_2\text{SnCl}_6$
848	plumbate	$\text{Na}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$	929	chloride dihydrate (ous)	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
849	salicylate	$\text{Na}(\text{C}_6\text{H}_4\text{OHCOO})$	930	iodide (ic)	SnI <sub>4</sub>
850	selenate	$\text{Na}_2\text{SeO}_4$	931	oxalate (ous)	$\text{SnC}_2\text{O}_4$
851	selenite	$\text{Na}_2\text{SeO}_3$	932	oxide (ous)	SnO
852	metasilicate	$\text{Na}_2\text{SiO}_3$	933	oxide (ic)	SnO <sub>2</sub>
853	metasilicate nonahydrate	$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	934	phosphate (ous)	$\text{Sn}_3(\text{PO}_4)_2$
854	aluminum silicate (albite)	$\text{NaAlSi}_3\text{O}_8$	935	sulfate (ic)	$\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$
855	stannate	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	936	sulfate (ous)	SnSO <sub>4</sub>
856	stearate	$\text{Na}(\text{C}_{17}\text{H}_{35}\text{COO})$	937	sulfide (ic)	SnS <sub>2</sub>
857	succinate	$(\text{CH}_2\text{COONa})_2 \cdot 6\text{H}_2\text{O}$	938	sulfide (ous)	SnS
858	sulfate (orthorhombic)	$\text{Na}_2\text{SO}_4$	939	tartrate (ous)	$\text{SnC}_4\text{H}_4\text{O}_6$
859	sulfate (heated)	$\text{Na}_2\text{SO}_4$	940	Titanium metal	Ti
860	sulfate (decahydrate)	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	941	carbide	TiC
861	hydrogen sulfate	$\text{NaHSO}_4$	942	fluoride	TiF <sub>4</sub>
862	hydrogen sulfate monohydrate	$\text{NaHSO}_4 \cdot \text{H}_2\text{O}$	943	potassium fluoride	$\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$
863	persulfate	$\text{Na}_2\text{S}_2\text{O}_8$	944	dioxide (anatase)	TiO <sub>2</sub>
864	sulfide nonahydrate	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	945	dioxide (rutile)	TiO <sub>2</sub>
865	sulfite	$\text{Na}_2\text{SO}_3$	946	Tungsten metal	W
866	sulfite heptahydrate	$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	947	acid (ic), (meta)	$\text{H}_2\text{W}_4\text{O}_{13}$
867	hyposulfite	$\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	948	trioxide (ic)	WO <sub>3</sub>
868	pyrosulfite	$\text{Na}_2\text{S}_2\text{O}_5$	949	Uranyl acetate	$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$
869	anthraquinone-β-sulfonate	$\text{C}_{14}\text{H}_9\text{O}_2\text{SO}_3\text{Na}$	950	Uranyl nitrate hexahydrate	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
870	naphthalene monosulfonate	$\text{C}_{10}\text{H}_7\text{SO}_3\text{Na}$	951	Vanadium	V
871	naphthalene α-disulfonate	$\text{C}_{10}\text{H}_6(\text{SO}_3\text{Na})_2$	952	carbide (14% C)	VC
872	tartrate	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	953	chloride	V <sub>2</sub> O <sub>3</sub>
873	hydrogen tartrate	$\text{NaHC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$	954	trioxide	V <sub>2</sub> O <sub>5</sub>
874	tellurite	$\text{Na}_2\text{TeO}_3$	955	pentoxide	$(\text{VO})_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$
875	thiocyanate	NaCNS	956	Vanadyl sulfate	
876	thiosulfate	$\text{Na}_2\text{S}_2\text{O}_3$	957	Yttrium nitrate	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
877	thiosulfate pentahydrate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	958	oxide	Y <sub>2</sub> O <sub>3</sub>
878	tungstate	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	959	Zinc metal	Zn
879	urate	$\text{Na}_2\text{C}_5\text{H}_2\text{O}_3\text{N}_4 \cdot \text{H}_2\text{O}$	960	acetate	$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$
880	metavanadate	$\text{NaVO}_3 \cdot \text{H}_2\text{O}$	961	acetate dihydrate	$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$
881	orthovanadate	$\text{Na}_3\text{VO}_4 \cdot 16\text{H}_2\text{O}$	962	aluminate	$\text{ZnAl}_2\text{O}_4$
882	Strontium	Sr	963	arsenate	$\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$
883	acetate	$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 1/2\text{H}_2\text{O}$	964	arsenite	$\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$
884	bromide hexahydrate	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	965	benzoate	$\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$
885	carbonate	$\text{SrCO}_3$	966	perchlorate	
886	chlorate	$\text{Sr}(\text{ClO}_3)_2 \cdot 8\text{H}_2\text{O}$	967	chloride (fused)	
887	chloride hexahydrate	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	968	chromate	$\text{ZnCrO}_4$
888	chromate	$\text{SrCrO}_4$	969	cyanide	$\text{Zn}(\text{CN})_2$
889	formate	$\text{Sr}(\text{HCO}_2)_2$	970	potassium cyanide	$\text{Zn}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$
890	formate dihydrate	$\text{Sr}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$	971	ferrocyanide	$\text{ZnF}_2$
891	fluoride	$\text{SrF}_2$	972	fluoride	$\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$
892	hydroxide octahydrate	$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	973	fluoride tetrahydrate	$\text{ZnI}_2$
893	iodide hexahydrate	$\text{SrI}_2 \cdot 6\text{H}_2\text{O}$	974	iodide	$\text{Zn}(\text{C}_6\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$
894	lactate	$\text{Sr}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$	975	lactate	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
895	nitrate	$\text{Sr}(\text{NO}_3)_2$	976	oxalate	ZnO
896	oxalate	$\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	977	oxide	$\text{ZnCo}_2\text{O}_4$
897	peroxide	$\text{SrO}_2$	978	cohalt oxide	$\text{ZnFe}_2\text{O}_4$
898	phosphate	$\text{SrHPO}_4$	979	iron oxide	$\text{Zn}(\text{MnO}_4)_2 \cdot 6\text{H}_2\text{O}$
899	salicylate	$\text{Sr}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$	980	permanganate	$\text{Zn}(\text{C}_6\text{H}_4\text{OHCOO})_2 \cdot 8\text{H}_2\text{O}$
900	sulfate	$\text{SrSO}_4$	981	phenolsulfonate	
901	tartrate	$\text{SrC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	982	phosphate	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$
902	Sulfur	S	983	phosphate tetrahydrate	$\text{ZnHPO}_3 \cdot 2 1/2\text{H}_2\text{O}$
903	Tantalum metal	Ta	984	phosphite	$\text{Zn}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
904	potassium fluoride	$\text{KTaF}_6$	985	hypophosphite	$\text{Zn}(\text{C}_6\text{H}_4\text{OHCOO})_2 \cdot 3\text{H}_2\text{O}$
905	pentoxide	$\text{Ta}_2\text{O}_5$	986	salicylate	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$
906	Tellurium	Te	987	sulfate monohydrate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
907	dichloride (ic)	$\text{TeCl}_2$	988	sulfate heptahydrate	$\text{ZnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
908	dioxide (ic)	$\text{TeO}_2$	989	ammonium sulfate	$\text{ZnSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
909	nitrate (ic) basic	$4\text{TeO}_2 \cdot \text{N}_2\text{O}_5 \cdot 1 1/2\text{H}_2\text{O}$	990	potassium sulfate	$\alpha\text{-ZnS}$
910	nitrate (ic)		991	sulfide (hexagonal)	$\beta\text{-ZnS}$
911	acid (ic)	$\text{H}_2\text{TeO}_4$	992	sulfide (cubic)	$\text{ZnSO}_3 \cdot 2 1/2\text{H}_2\text{O}$
912	acid dihydrate (ic)	$\text{Te}(\text{OH})_6$	993	sulfide	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$
913	Thallium metal (hexagonal)	$\alpha\text{-Tl}$	994	valerate	
914	chloride (ous)	$\text{TlCl}$	995	Zirconium metal	Zr
915	nitrate (ic)	$\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	996	Zirconyl chloride	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$
916	oxide (ic)	$\text{Tl}_2\text{O}_3$	997	Zirconium nitrate	$\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$
917	sulfate (ous)	$\text{Tl}_2\text{SO}_4$	998	dioxide (monoclinic)	$\text{ZrO}_2$
918	Thorium metal	Th	999	silicate	$\text{ZrSiO}_4$
919	acetate		1000	Zirconyl sulfate	
920	chloride	$\text{ThCl}_4$			



(Starred patterns were checked with published crystal structure data. B = broad line)

(Starred patterns were checked with published crystal structure data. B = broad line)

[illegible]



(Starred patterns were checked with published crystal structure data)

[illegible]



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
57. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> *		62. NH <sub>4</sub> CNS		67. Sb*		71. SbCl <sub>3</sub>		76. Sb <sub>2</sub> O <sub>3</sub>		81. (SbO)KC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> - 1/2H <sub>2</sub> O	
5.2	0.20	9.0	0.10	3.71	0.15	8.0	0.30	6.0	1.00	6.8	0.83
4.36	1.00	6.3	0.10	3.10	1.00	5.0	1.00	3.10	0.80	5.8	0.58
3.91	0.20	5.3	0.10	2.24	0.63	4.69	0.30	2.97	0.80	4.73	0.50
3.12	0.40	4.15	0.60	2.14	0.63	4.10	0.30	2.58	0.16	3.90	0.42
3.03	0.40	3.66	1.00	1.86	0.15	3.44	0.50	2.36	0.04	3.64	1.00
2.67	0.07	3.41	0.20	1.76	0.44	3.08	0.50	1.98	0.16	3.38	0.33
2.51	0.07	3.31	0.60	1.55	0.20	2.80	0.40	1.82	0.50	3.14	0.20
2.32	0.20	3.11	0.80	1.470	0.13	2.63	0.30	1.73	0.16	2.96	0.23
2.18	0.20	2.99	0.70	1.410	0.20	2.50	0.40	1.55	0.36	2.87	0.23
2.05	0.01	2.93	0.70	1.360	0.25	2.20	1.00	1.480	0.08	2.75	0.23
1.97	0.04	2.72	0.50	1.310	0.08	2.04	0.40	1.440	0.08	2.59	0.13
1.93	0.02	2.60	0.40	1.258	0.15	1.88	0.50	1.340	0.12	2.50	0.27
1.77	0.02	2.47	0.10	1.243	0.10	1.71	0.75	1.180	0.08	2.42	0.07
1.73	0.02	2.42	0.40	1.215	0.03	1.66	0.25	1.150	0.04	2.30	0.17
1.70	0.02	2.33	0.10	1.190	0.03	1.60	0.25	1.075	0.04	2.19	0.23
1.63	0.05	2.22	0.10	1.120	0.03	1.57	0.25	1.048	0.04	2.06	0.07
1.56	0.02	2.08	0.20	1.075	0.10	1.54	0.25	0.990	0.04	1.99	0.20
1.52	0.02	1.99	0.10	1.047	0.03	1.50	0.35			1.96	0.20
1.490	0.05	1.91	0.10	1.031	0.08	1.410	0.05			1.91	0.10
						1.380	0.05	77. K <sub>2</sub> S.Sb <sub>2</sub> S <sub>3</sub>		1.86	0.13
						1.350	0.05	(4)	0.40	1.81	0.10
						1.310	0.05	(10)	1.00	1.77	0.10
						1.240	0.30		0.10	1.65	0.07
58. (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> *		63. (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub>		68. SbAsO <sub>4</sub>		72. SbOCl		(2)	0.20	1.61	0.07
5.6	0.50	5.0	0.32	6.4	0.12	13.2	0.05		0.10	1.57	0.07
5.0	0.50	4.75	0.56	4.54	0.02	9.0	0.05		0.10	1.51	0.10
4.02	0.45	4.58	0.80	4.21	0.02	6.2	0.30		0.10	1.470	0.07
3.52	0.75	3.91	0.16	3.68	0.20	4.80	0.05		0.10	1.340	0.03
3.35	1.00	3.46	0.08	3.49	0.35	4.03	0.20		0.10	1.260	0.03
3.13	0.50	3.34	0.08	3.22	1.00	3.70	0.20	78. Sb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		1.213	0.07
3.03	0.05	3.20	0.08	3.13	0.25	3.27	0.05		0.20		
2.93	0.30	3.02	1.00	2.79	0.35	3.10	1.00	(20)	5.4		
2.85	0.15	2.77	0.08	2.55	0.08	2.81	0.63	(12.5)	5.2		
2.61	0.05	2.62	0.72	2.47	0.08	2.64	0.05		4.25		
2.51	0.05	2.36	0.16	2.40	0.06	2.55	0.05		3.45		
2.47	0.35	2.27	0.08	2.27	0.04	2.37	0.40	(8)	3.30		
2.41	0.10	2.18	0.08	2.13	0.02	2.25	0.10		3.15		
2.31	0.15	1.95	0.08	2.05	0.02	2.12	0.05		2.90		
2.21	0.25	1.81	0.24	1.97	0.60	2.04	0.10		2.80		
2.02	0.20	1.72	0.16	1.92	0.02	1.98	0.25		2.69		
1.93	0.15	1.69	0.08	1.81	0.02	1.86	0.10		2.61		
1.86	0.05	1.56	0.08	1.73	0.02	1.79	0.05		2.46		
1.77	0.05	1.440	0.08	1.68	0.60	1.65	0.05		2.41		
1.71	0.10			1.61	0.12	1.54	0.05		2.34		
1.65	0.05			1.57	0.18	1.480	0.10		2.27		
1.59	0.05			1.475	0.02				2.13		
1.53	0.05			1.40	0.06				2.04		
				1.367	0.06				1.97		
				1.280	0.18				1.89		
				1.250	0.12				1.82		
				1.183	0.02				1.78		
				1.140	0.08				1.70		
				1.075	0.12				1.65		
				1.042	0.02				1.57		
				0.973	0.02				1.51		
				0.943	0.06				1.475		
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TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>
86. As <sub>2</sub> S <sub>3</sub>		91. Ba(ClO <sub>3</sub> ) <sub>2</sub>		94. BaCl <sub>2</sub>		98. Ba(CN) <sub>2</sub>		102. Ba(HCO <sub>2</sub> ) <sub>2</sub>		105. BaMnO <sub>4</sub>			
4.82	(15)	1.00	7.0	0.13	4.05	(25)	0.83	9.4	(62.5)	1.00	5.8	4.42	0.07
4.42		0.07	5.7	0.25	3.88		0.13	6.9		0.24	5.4	3.97	0.33
4.00	(7)	0.47	5.2	0.08	3.72		0.07	4.80		0.13	4.42	3.68	0.20
3.70		0.47	4.37	0.15	3.07		0.50	4.40		0.24	3.80	3.50	(30) 1.00
3.19		0.20	4.20	0.13	2.89		0.50	3.68		0.13	3.34	3.40	0.42
3.05		0.13	3.78	0.05	2.80		0.50	3.50		0.24	3.11	(25) 0.83	0.50
2.85		0.47	3.58	(40) 1.00	2.63		0.33	3.37	(40)	0.64	2.92	3.16	0.30
2.70	(8)	0.53	3.34	(30) 0.75	2.48		0.23	3.08		0.32	2.75	2.89	0.30
2.55		0.07	3.23	0.50	2.33	(30)	1.00	2.94	(30)	0.48	2.66	2.53	0.03
2.45		0.47	2.89	0.38	2.18		0.07	2.73		0.10	2.54	2.35	0.03
2.31		0.13	2.80	0.50	2.02	(25)	0.83	2.63		0.16	2.44	2.24	0.03
2.12		0.13	2.60	0.03	1.85		0.07	2.46		0.24	2.30	2.15	(25) 0.83
2.07		0.13	2.38	0.18	1.79		0.10	2.40		0.10	2.21	1.96	0.03
2.02		0.07	2.33	0.18	1.65		0.58	2.33		0.16	2.10	1.91	0.13
1.91		0.13	2.19	(25) 0.63	1.52		0.83	2.20		0.24	2.02	1.80	0.03
1.85		0.13	2.10	0.10	1.450		0.07	2.06		0.16	1.92	1.71	0.23
1.74		0.13	2.03	0.05	1.415		0.17	1.99		0.32	1.85	1.65	0.03
1.68		0.27	1.99	0.31	1.340		0.33	1.92		0.28	1.79	1.61	0.03
1.64		0.07	1.89	0.20	1.275		0.33	1.87		0.03	1.67	1.56	0.13
87. Ba*			1.82	0.13	1.210		0.13	1.78		0.03	1.62		
			1.75	0.18	1.168		0.17	1.73		0.03	1.57		
3.54	(40)	1.00	1.67	0.08	1.117		0.17	1.69		0.20	1.461		
2.51	(20)	0.50	1.64	0.05	1.040		0.13	1.59		0.03	1.411		
2.04	(40)	1.00	1.54	0.23	1.010		0.17	1.56		0.06	1.375	5.7	0.38
1.77		0.50	1.52	0.03				1.52		0.05	1.332	3.68	(25) 0.63
1.58		0.50	1.50	0.03				1.485		0.02	1.305	3.39	(40) 1.00
1.443		0.05	1.443	0.08	95. BaCl <sub>2</sub> ·2H <sub>2</sub> O			1.446		0.10	1.274	3.31	(30) 0.71
1.340		0.44	1.411	0.13	5.5	0.50		1.382		0.10	1.260	2.95	0.15
1.181		0.15			4.98	0.33		1.341		0.03	1.220	2.84	0.63
1.120		0.05			4.48	(30) 1.00		1.288		0.08	1.187	2.38	0.15
1.066		0.03	92. Ba(ClO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O		3.64	0.42		1.254		0.05	1.151	2.24	0.63
1.022		0.03	6.0	(62.5) 1.00	3.39	0.50		1.215		0.05	1.130	2.20	0.38
0.981		0.08	4.70	0.02	3.21	0.33		1.180		0.03	1.100	2.05	0.10
0.915		0.03	3.70	0.24	2.91	(30) 1.00		1.149		0.06		1.92	0.31
88. Ba(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O			3.35	(40) 0.64	2.70	0.50						1.85	0.18
9.3	(40)	1.00	3.14	0.40	2.54	(20) 0.66			103. Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O			1.80	0.15
7.0		0.38	3.00	0.24	2.40	0.33		99. BaF <sub>2</sub> *		6.6	0.50	1.74	0.10
4.88		0.15	2.90	0.48	2.23	0.33	3.58	(125) 1.00		6.0	(25) 1.00	1.65	0.31
4.43		0.38	2.78	0.02	2.08	0.58	3.09	0.25		5.5	0.32	1.57	0.15
3.55		0.25	2.50	0.32	2.00	0.33	2.19	(125) 1.00		4.62	(15) 0.60	1.475	0.15
3.40	(30)	0.75	2.32	(50) 0.80	1.70	0.10	1.86	(100) 0.80		4.33	0.50	1.440	0.08
3.10	(17.5)	0.44	2.21	0.32	1.60	0.12	1.78	0.15		4.13	0.08	1.375	0.08
2.76		0.10	2.12	0.20	1.56	0.17	1.55	0.15		3.92	0.24	1.332	0.08
2.65		0.10	2.01	0.13	1.52	0.16	1.420	0.32		3.71	0.12	1.294	0.08
2.49		0.25	1.94	0.10	1.450	0.07	1.382	0.18		3.53	0.32	1.258	0.10
2.34		0.20	1.85	0.13	1.385	0.10	1.262	0.32		3.38	0.16		
2.21		0.25	1.80	0.24	1.340	0.03	1.190	0.20		3.22	0.50	107. Ba(NO <sub>3</sub> ) <sub>2</sub> *	
2.07		0.25	1.73	0.14	1.305	0.10	1.095	0.05		3.07	0.32	4.69	(75) 0.75
2.00		0.38	1.66	0.13			1.045	0.15		3.00	0.32	4.06	0.30
1.93		0.38	1.61	0.02	96. BaCrO <sub>4</sub>		1.031	0.03		2.78	(15) 0.60	3.62	0.15
1.70		0.31	1.57	0.02			0.978	0.06		2.73	0.32	3.31	0.10
1.450		0.18	1.52	0.10	4.50	0.11	0.944	0.03		2.66	0.60	2.87	0.40
1.390		0.18	1.470	0.10	4.00	0.27	0.933	0.02		2.56	0.16	2.44	(100) 1.00
1.290		0.15	1.440	0.10	3.54	0.40	0.866	0.03		2.37	0.16	2.34	(50) 0.50
1.260		0.10	1.390	0.10	3.19	(62.5) 0.83	0.859	0.02		2.30	0.40	2.02	0.20
1.225		0.08	1.320	0.10	2.90	0.33	0.827	0.05		2.17	0.20	1.86	0.40
1.185		0.08	1.290	0.06	2.78	0.27				2.12	0.20	1.81	0.30
1.185		0.08	1.270	0.06	2.53	0.08	100. BaTiF <sub>6</sub>			2.07	0.50	1.65	0.30
1.093		0.08	1.190	0.10	2.37	0.07				2.02	0.16	1.56	0.30
89. Barium Borate			1.170	0.06	2.25	0.07	4.79	0.11		1.97	0.16	1.433	0.15
9.0		0.08			2.16	(75) 1.00	3.68	(62.5) 1.00		1.93	0.12	1.370	0.40
6.3		0.10	93. Ba(ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O		1.97	0.01	3.15	(40) 0.64		1.81	0.20	1.351	0.10
5.2		0.15	6.4	0.20	1.91	0.17	2.40	0.16		1.74	0.08	1.318	0.01
4.53	(25)	0.63	4.87	0.27	1.80	0.10	2.28	0.40		1.67	0.20	1.281	0.08
3.70		0.15	4.87	0.09	1.71	0.33	2.12	0.06		1.63	0.04	1.238	0.13
3.41	(30)	0.75	3.84	0.67	1.66	0.11	2.00	(40) 0.64		1.59	0.12	1.222	0.13
3.20		0.25	3.65	(50) 0.67	1.62	0.11	1.84	0.10		1.55	0.08	1.170	0.04
3.00	(40)	1.00	2.90	(75) 1.00	1.56	0.23	1.74	0.05		1.468	0.24	1.137	0.10
2.72		0.50	2.64	0.13	1.50	0.05	1.58	0.06				1.126	0.06
2.62		0.15	2.39	0.20	1.450	0.13	1.450	0.14				1.085	0.13
2.50		0.15	2.25	0.27	1.410	0.03	1.390	0.05				1.056	0.20
2.32		0.15	2.14	(30) 0.40	1.380	0.07	1.355	0.03	104. Ba(IO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O		6.0	0.50	
2.26		0.63	2.10	0.08	1.350	0.03	1.262	0.03		4.52	0.32	108. Ba(NO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	
2.12		0.50	2.00	0.11	1.325	0.03	1.230	0.02		4.00	0.44	6.1	0.44
2.06		0.38	1.92	0.33	1.288	0.13	1.200	0.05		3.70	0.44	5.1	(30) 0.75
1.97		0.15	1.82	0.13	1.250	0.04	1.						







TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
140. Bismuth Osmate		145. Bi <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> OHCOO) <sub>3</sub>		150. Cd(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O		154. CdCl <sub>2</sub> ·2 <sup>1</sup> / <sub>2</sub> H <sub>2</sub> O		158. CdC <sub>2</sub> O <sub>4</sub>		161. CdFe <sub>2</sub> O <sub>4</sub> *	
10.6	(10) 0.80	16.0	(30) 1.00	11.8	0.25	7.3	(25) 0.63	8.0	0.04	3.08	(17.5) 0.58
9.4	(10) 0.80	7.5	0.07	9.9	1.00	5.9	(40) 1.00	6.5	0.20	2.62	(30) 1.00
6.2	0.32	6.8	0.13	8.6	(15) 0.75	4.65	0.31	5.7	1.00	2.52	0.17
5.5	0.32	6.2	(10) 0.33	7.7	0.20	3.63	0.44	4.69	0.07	2.19	0.07
4.80	(12.5) 1.00	4.95	0.10	7.1	0.30	3.37	0.50	4.50	0.30	2.00	0.03
3.94	0.08	4.48	0.10	6.2	0.10	2.84	0.13	3.98	0.07	1.78	0.20
3.20	0.08	3.98	(7) 0.23	5.6	0.40	2.62	(40) 1.00	3.70	(40) 0.40	1.67	(12.5) 0.42
3.01	0.48	3.40	0.03	5.2	0.20	2.42	0.38	3.22	0.15	1.54	0.42
2.78	0.32	3.13	0.03	4.84	0.30	2.35	0.31	3.08	0.15	1.489	0.07
2.62	0.08	2.75	0.03	4.55	0.40	2.08	0.23	2.85	(40) 0.40	1.455	0.07
2.41	0.64	2.52	0.03	4.00	0.35	1.97	0.50	2.73	0.40	1.377	0.07
1.97	0.40	2.40	0.03	3.76	0.40	1.88	0.44	2.65	0.20	1.329	0.10
1.83	0.24	2.26	0.03	3.56	0.40	1.81	0.15	2.56	0.07	1.313	0.10
1.79	0.24	2.08	0.07	3.35	0.20	1.76	0.10	2.49	0.07	1.259	0.03
1.66	0.48	2.02	0.03	3.25	(10) 0.50	1.68	0.15	2.41	0.02	1.165	0.13
1.61	0.16	1.93	0.03	3.12	0.10	1.64	0.15	2.33	0.20	1.135	0.17
1.52	0.40	1.72	0.03	3.00	0.10	1.60	0.10	2.25	0.07	162. Cd <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	
1.467	0.16	1.62	0.03	2.96	0.10	1.50	0.15	2.21	0.07	8.5	(4) 0.67
1.394	0.16			2.90	0.10	1.450	0.08	2.13	0.06	7.4	0.33
1.342	0.16	146. Bi <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		2.77	0.15	1.390	0.05	2.04	0.13	7.0	0.33
1.250	0.16	5.6	(6) 0.75	2.66	0.10	1.330	0.08	1.98	0.20	6.6	0.33
1.202	0.24	5.2	(6) 0.75	2.45	0.05	1.250	0.08	1.90	0.10	6.0	0.33
1.180	0.24	4.30	(8) 1.00	2.40	0.05	1.193	0.10	1.85	0.10	4.68	(4) 0.67
1.108	0.32	3.36	0.37	2.29	0.05	1.153	0.05	1.81	0.13	4.21	(6) 1.00
141. Bi <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>		3.13	0.50	2.20	0.15	1.103	0.10	1.74	0.04	3.22	0.67
9.9	0.20	2.94	0.13	2.09	0.20			1.70	0.03	3.08	0.67
6.4	(20) 1.00	2.74	0.13	2.02	0.10	155. Cd(OH) <sub>2</sub> *		1.65	0.07	2.95	0.67
5.6	0.10	2.62	0.25	1.98	0.10	4.70	(100) 1.00	1.58	0.06	2.77	0.17
5.1	0.30	2.45	0.13	1.92	0.10	3.02	(62.5) 0.63	1.53	0.04	2.68	0.33
4.79	0.10	2.36	0.13	1.83	0.10	2.55	(100) 1.00	1.50	0.06	2.50	0.17
4.17	(8) 0.40	2.17	0.25	1.72	0.10	1.86	0.40	1.473	0.07	2.38	0.17
3.81	0.30	2.07	0.25			1.74	0.30	1.420	0.03	2.23	0.17
3.61	0.10	1.99	0.13	151. Cd(BrO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O		1.63	0.30	1.358	0.06	2.09	0.17
3.45	0.30	1.91	0.13	6.2	0.08	1.51	0.13	1.310	0.04	2.02	0.17
3.22	0.15	1.87	0.13	5.6	0.08	1.440	0.20	1.275	0.02	1.97	0.17
3.09	0.05	1.71	0.13	4.40	(12.5) 1.00	1.400	0.20	1.237	0.08	1.89	0.17
3.00	0.10	1.67	0.13	4.00	0.08	1.271	0.15	1.201	0.03	1.85	0.17
2.88	0.20	1.60	0.13	3.71	0.08	1.165	0.07	1.161	0.04	1.78	0.33
2.82	0.20	1.53	0.13	3.51	0.08	1.139	0.08	1.137	0.02	1.74	0.33
2.76	0.15	1.490	0.13	3.17	(6) 0.48	1.110	0.13	1.120	0.04	1.68	0.33
2.62	0.30	1.440	0.13	3.08	(4) 0.32	1.090	0.03			1.62	0.50
2.52	0.10	1.360	0.13	2.81	0.08	1.028	0.10	159. CdC <sub>2</sub> O <sub>4</sub> ·3H <sub>2</sub> O		163. Cd(C <sub>6</sub> H <sub>5</sub> OHCOO) <sub>2</sub> ·H <sub>2</sub> O	
2.40	(7) 0.35	1.225	0.13	2.74	0.08	1.005	0.03	6.5	0.05	16.0	(75) 1.00
2.17	0.30			2.49	0.08	0.980	0.04	5.7	(50) 0.40	10.0	0.09
2.08	0.35	147. H <sub>3</sub> BO <sub>3</sub>		2.37	0.16	0.925	0.05	4.90	0.16	6.6	(15) 0.20
2.00	0.15	5.9	(17.5) 0.28	2.26	0.08			4.51	0.06	6.3	0.13
1.91	0.20	3.16	(62.5) 1.00	2.19	0.32	156. 2KI.CdI <sub>2</sub> ·2H <sub>2</sub> O		3.75	(125) 1.00	5.8	0.05
1.85	0.15	2.90	0.03	2.05	0.32	7.3	0.08	3.42	0.05	5.2	0.03
1.80	0.20	2.81	0.02	1.93	0.16	5.9	0.32	3.20	0.12	4.80	0.11
1.73	0.10	2.62	0.06	1.81	0.16	4.25	(12.5) 1.00	3.07	0.02	4.55	0.05
1.70	0.05	2.55	0.02	1.69	0.16	3.60	(8) 0.64	2.85	0.08	4.22	0.07
1.63	0.05	2.49	0.02	1.370	0.16	3.45	0.48	2.72	0.14	3.98	0.04
1.60	0.15	2.23	(8) 0.13	152. CdCO <sub>3</sub> *		3.16	0.48	2.66	(50) 0.24	3.82	(20) 0.26
1.52	0.10	2.16	0.03	3.77	(25) 0.80	2.54	0.64	2.45	0.05	3.65	0.20
1.486	0.08	2.08	0.06	2.94	(30) 1.00	2.37	0.08	2.37	0.06	3.45	0.13
1.435	0.15	2.02	0.03	2.46	0.50	2.70	0.08	2.31	0.24	3.24	0.07
1.390	0.10	1.68	0.02	2.23	0.03	2.27	0.16	2.22	0.06	3.10	0.07
142. Bi <sub>2</sub> O <sub>3</sub>		1.63	0.03	2.06	0.45	2.19	(12.5) 1.00	2.13	0.02	2.87	0.03
3.42	0.05	1.58	0.03	1.88	0.33	2.02	0.08	2.02	0.16	2.51	0.05
3.25	(20) 1.00	148. B <sub>2</sub> C		1.83	(25) 0.80	1.93	0.48	1.93	0.32	2.41	0.03
2.69	(17.5) 0.88	4.00	0.05	1.58	0.40	1.85	0.08	1.87	0.24	2.34	0.05
2.54	0.05	3.79	0.15	1.50	0.17	1.72	0.08	1.79	0.12	2.22	0.03
2.39	0.15	3.39	(40) 1.00	1.470	0.05	1.58	0.16	1.76	0.16	2.06	0.04
2.03	0.05	2.57	0.23	1.355	0.05			1.67	0.12	1.99	0.04
1.95	(5) 0.25	2.38	(15) 0.38	1.295	0.05	157. Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O		1.59	0.04	1.92	0.03
1.87	0.15	2.03	(15) 0.38	1.260	0.17	6.5	0.30	1.55	0.08		
1.82	0.05	1.81	0.03	1.230	0.05	5.0	(50) 1.00	1.50	0.14	164. 3CdSO <sub>4</sub> ·8H <sub>2</sub> O	
1.75	0.20	1.69	0.03	1.190	0.08	4.40	(30) 0.60	1.450	0.06	4.90	(40) 0.80
1.66	0.10	1.54	0.03	1.142	0.08	3.65	(25) 0.50	1.417	0.01	3.70	0.20
1.58	0.10	1.50	0.03	1.120	0.08	3.39	0.02	1.385	0.08	3.55	(50) 1.00
1.490	0.05	1.450	0.05	1.022	0.08	3.23	0.16	1.359	0.03	3.20	0.60
1.395	0.05	1.400	0.05	0.976	0.07	3.06	0.02	1.338	0.05	3.10	0.16
1.305	0.05	1.320	0.05	0.942	0.07	2.99	0.16	1.315	0.10	2.51	(40) 0.80
1.270	0.05	1.260	0.03	0.880	0.07	2.92	0.50	1.272	0.08	2.38	0.60
1.225	0.05	1.230	0.05			2.66	0.30	1.247	0.05	2.30	0.35
1.195	0.05	1.158	0.05	153. CdCl <sub>2</sub> *		2.40	0.20	1.228	0.03	2.10	0.25
1.120	0.05			5.8	(50) 1.00	2.55	0.16	1.212	0.02	2.05	0.25
143. Bi <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O				3.27	(30) 0.60	2.40	0.40			1.94	0.12
3.73	0.17	149. Cd									



(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I/I<sub>i</sub></i>	<i>d</i>	<i>I/I<sub>i</sub></i>	<i>d</i>	<i>I/I<sub>i</sub></i>	<i>d</i>	<i>I/I<sub>i</sub></i>	<i>d</i>	<i>I/I<sub>i</sub></i>	<i>d</i>	<i>I/I<sub>i</sub></i>	<i>d</i>	<i>I/I<sub>i</sub></i>	<i>d</i>	<i>I/I<sub>i</sub></i>	
166. Ca*		171. 5CaO.3Al <sub>2</sub> O <sub>3</sub> *		175. Calcium Borate		180. CaCO <sub>3</sub> *		184. CaCl <sub>2</sub> .2H <sub>2</sub> O		189. CaCrO <sub>4</sub> *						
3.21	(40)	1.00	4.95	(20)	0.67	5.8	0.07	3.86	0.08	6.1	0.40	4.80		0.06		
2.80	(12.5)	0.30	3.19		0.20	3.40	(12.5)	0.42	3.04	(125)	1.00	4.34		0.50	3.63	
1.97	(8)	0.20	3.01		0.23	3.04	(30)	1.00	2.49		0.20	3.05	(17.5)	0.70	2.90	
1.68		0.20	2.68	(30)	1.00	2.90		0.23	2.28	(30)	0.24	2.82	(25)	1.00	2.70	
1.61		0.10	2.44	(15)	0.50	2.76		0.07	2.09		0.20	2.68		0.16	2.57	
1.28		0.05	2.19		0.50	2.62		0.33	1.92	(40)	0.32	2.51		0.20	2.39	
1.246		0.03	1.94		0.50	2.25		0.07	1.87		0.24	2.35		0.20	2.27	
1.138		0.05	1.73		0.13	2.14	(12.5)	0.42	1.60		0.16	2.26		0.16	1.86	
			1.66		0.42	2.01		0.03	1.51		0.12	2.16		0.24	1.81	
			1.59		0.50	1.95		0.42	1.475		0.05	2.12	(15)	0.60	1.62	
			1.52		0.13	1.86		0.33	1.439		0.08	2.01		0.08	1.58	
			1.478		0.10	1.70		0.10	1.425		0.05	1.87		0.20	1.50	
11.0	(50)	1.00	1.395		0.27	1.65		0.07	1.350		0.03	1.78		0.12	1.45	
8.5	(10)	0.20	1.344		0.10	1.51		0.13	1.295		0.05	1.71		0.12	1.345	
6.7		0.06	1.309		0.17	1.310		0.07	1.243		0.03	1.67		0.16	1.293	
5.9		0.12	1.261		0.07	1.200		0.03	1.179		0.03	1.62		0.04	1.210	
5.5		0.10	1.236		0.07	1.070		0.03	1.150		0.05	1.52		0.04	1.188	
3.80		0.08	1.209		0.10				1.045		0.06	1.475		0.16	1.154	
3.58		0.08	1.174		0.10				1.011		0.03	1.405		0.04	1.130	
3.34	(25)	0.50	1.141		0.07	176. CaBr <sub>2</sub> .6H <sub>2</sub> O*									1.027	
3.13		0.16	1.112		0.13	4.03	(25)	1.00	181. Ca(ClO <sub>3</sub> ) <sub>2</sub> .2H <sub>2</sub> O		185. CaCl <sub>2</sub> .4H <sub>2</sub> O			1.000	0.08	
2.96		0.08	1.091		0.03	3.49	(12.5)	0.50			6.0		0.27	0.973		
2.68		0.18				2.85		0.50			5.2		0.20			
2.34		0.10	172. Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>			2.65		0.50	6.0	0.30	4.70	(12.5)	0.42	190. CaCrO <sub>4</sub> .2H <sub>2</sub> O		
2.23		0.16	8.7		0.16	2.34		0.50	5.6	0.12	3.58		0.27	8.0	(15)	
2.15		0.16	6.0		0.04	2.21	(15)	0.60	5.4	0.12	3.30		0.13	4.30	(30)	
2.03		0.08	5.5		0.04	2.01		0.16	4.68		0.14	3.02	0.13	4.02	0.07	
1.97		0.16	4.90		0.04	1.92		0.08	4.30	(25)	0.50	2.94	0.13	3.90	0.07	
1.88		0.08	4.01		0.40	1.80		0.16	3.62		0.06	2.81	0.42	3.66	0.23	
1.84		0.20	3.51	(12.5)	0.50	1.75		0.24	3.30		0.10	2.72	0.27	3.11	(20)	
1.66		0.04	3.22		0.04	1.60		0.16	3.05	(30)	0.60	2.63	1.00	2.94	0.67	
1.52		0.04	3.05		0.20	1.53		0.24	2.94		0.12	2.39	0.42	2.70	0.42	
			2.90	(25)	1.00	1.495		0.08	2.80	(50)	1.00	2.22	(20)	0.67	0.30	
			2.82	(20)	0.80	1.430		0.16	2.70		0.10	2.16		0.13	0.13	
10.0	(75)	1.00	2.69		0.16	1.395		0.04	2.64		0.16	2.08		0.20	0.03	
6.7	(10)	0.11	2.34		0.12	1.353		0.08	2.48		0.14	2.00		0.27	0.17	
6.0		0.13	2.30		0.12	1.312		0.04	2.37		0.18	1.91		0.07	0.10	
5.2		0.05	2.22		0.16	1.285		0.04	2.32		0.06	1.75		0.13	0.07	
4.10		0.08	2.00		0.28	1.259		0.08	2.26		0.08	1.70		0.07	0.03	
3.78		0.08	1.88		0.50	1.219		0.08	2.20		0.04	1.62		0.07	0.07	
3.61	(40)	0.01	1.75		0.16	1.190		0.04	2.16		0.10	1.57		0.07	0.20	
3.28		0.53	1.69		0.20				2.10		0.30	1.49		0.13	0.07	
2.97		0.09	1.65		0.08	177. CaC <sub>2</sub> I*			1.99		0.08			1.87	0.13	
2.89		0.11	1.52		0.12	3.32		0.25	1.92		0.04	186. CaCl <sub>2</sub> .6H <sub>2</sub> O		1.82	0.10	
2.72		0.04	1.485		0.24	3.18	(20)	0.50	1.87		0.10	6.9		0.15		
2.41		0.11				2.74	(40)	1.00	1.85		0.10	3.93	(30)	0.75	191. CaCr <sub>2</sub> O <sub>7</sub>	
2.33		0.11	173. Calcium Arsenite			2.08	(17.5)	0.44	1.77		0.08	3.41		0.31	7.0	(9)
2.23		0.03				1.93		0.31	1.70		0.04	2.78	(25)	0.63	6.4	0.07
2.17		0.07	9.0		0.48	1.86		0.25	1.66		0.10	2.58		0.50	5.3	0.27
2.08		0.11	4.97		0.32	1.67		0.18	1.62		0.04	2.27		0.50	4.98	0.27
1.97		0.09	4.49	(8)	0.64	1.375		0.08	1.50		0.04	2.16	(40)	1.00	4.20	0.07
1.87		0.05	3.54		0.16	1.348		0.08	1.470		0.12	1.97		0.50	4.08	0.07
1.81		0.05	3.05	(12.5)	1.00	1.263		0.05	1.402		0.08	1.90		0.15	3.90	(15)
			2.85		0.40	1.232		0.08	1.321		0.06	1.76		0.13	3.73	0.53
			2.65	(7)	0.56	1.147		0.05				1.70		0.38	3.50	(12.5)
			2.56		0.16	1.028		0.03				1.57		0.10	3.39	0.83
			2.09		0.16				182. CaCl <sub>2</sub> *			1.489		0.38	3.08	0.53
3.09		0.18	2.01		0.16	178. CaC <sub>2</sub> II*			4.49	(25)	1.00	1.452		0.20	2.98	0.40
2.83	(30)	0.60	1.94		0.16				3.46		0.16	1.393		0.15	2.78	0.53
2.70	(50)	1.00	1.81		0.56	3.49		0.20	3.05	(20)	0.80	1.365		0.05	2.62	0.27
2.42		0.04	1.69		0.24	3.32		0.16	2.85	(15)	0.32	1.313		0.13	2.39	0.53
2.33		0.02	1.52		0.16	3.17		0.16	2.33		0.60	1.290		0.10	2.30	0.27
2.25		0.02	1.425		0.08	2.93	(62.5)	1.00	2.24		0.16	1.225		0.15	2.20	0.27
2.18	(30)	0.60	1.315		0.08	2.79	(25)	0.40	2.09		0.16	1.189		0.10	2.06	0.13
2.07		0.20	1.230		0.08	2.28		0.14	1.90		0.36	1.170		0.10	1.99	0.13
1.99		0.35	1.115		0.08	2.09		0.24	1.79		0.08	1.079		0.13	1.93	0.33
1.73		0.30				2.06		0.16	1.68		0.12	1.006		0.10	1.78	0.40
1.59		0.08				2.00		0.13	1.56		0.04				1.74	0.40
1.55		0.25	174. Ca(C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>2</sub> .3H <sub>2</sub> O			1.95	(17.5)	0.28	1.51		0.08	187. CaCl <sub>2</sub> .CaF <sub>2</sub>				
1.51		0.02	6.4		0.07	1.88		0.08	1.490		0.04	6.8		0.04	192. Ca <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ) <sub>2</sub> .4H <sub>2</sub> O	
1.47		0.20	5.8		0.13	1.80		0.20	1.330		0.12	3.39		0.08	15.3	(6)
1.425		0.02	5.3	(7)	0.47	1.76		0.10	1.243		0.12	3.18	(25)	0.50	3.95	(4)
1.395		0.06	4.41		0.33	1.71		0.06	1.210		0.12	2.75	(50)	1.00	3.09	(4)
1.340		0.25	4.22	(12.5)	0.83	1.67		0.08	1.165		0.04	2.56		0.40	2.98	0.33
1.236		0.04	3.98		0.07	1.59		0.05				1.94	(25)	0.50	2.78	0.17
1.175		0.08	3.48	(15)	1.00	1.52		0.05				1.75		0.02	2.58	0.33
			2.97		0.27	1.470		0.05	5.9	(10)	0.40	1.68		0.02	2.39	0.17
			2.67		0.27	1.300		0.13	4.38		0.12	1.55		0.25	2.23	0.33
4.08		0.20	2.54		0.07	179. CaC <sub>2</sub> III			3.41		0.12	1.450		0.02	2.03	0.33
3.30		0.04	2.48		0.07	3.52		0.60	3.22		0.24	1.374		0.12	1.96	0.17
2.68	(25)	1.00	2.30		0.07	3.20		0.10	3.03		0.40	1.215		0.08	1.81	0.17
2.39		0.04	2.23		0.07	2.92	(8)	0.80	2.81		0.24	1.155		0.04	1.75	0.17
2.19		0.08	2.12		0.07	2.86	(10)	1.00	2.55	(25)	1.00	1.115		0.02	1.66	0.17
2.03		0.04	2.06		0.07	2.27		0.40	2.40		0.24	1.028		0.04		
1.90	(6)	0.24	2.01		0.07	2.15		0.20	2.26	(15)	0.60	0.973		0.02		
1.55	(6)	0.24	1.98		0.07	2.05	(8)	0.80	2.17		0.04	0.910		0.02		
1.342		0.12	1.93		0.07	1.93		0.60	2.11		0.28	0.871		0.02	193. CaCN <sub>2</sub>	
1.203		0.08	1.87		0.07	1.78		0.60	1.93		0.12				4.90	(4)
1.015		0.04						0.60	1.60		0.12	188. Ca(ClO) <sub>2</sub> .4H <sub>2</sub> O			3.36	0.20
									1.53		0.08	4.95		0.25	3.03	(10)
									1.50		0.12	3.18	(25)	0.63	2.62	(8)
									1.460		0.04	2.47		0.05	2.50	0.10
									1.410		0.04	2.36	(40)	1.00	2.29	0.10
									1.360		0.12	1.93	(20)	0.50	2.08	0.10







TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>
219. $\text{Ca}(\text{H}_2\text{PO}_4)_2^*$		222. $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$		227. $\text{Ca}_3\text{P}_2$		231. $\text{CaSiO}_3$		235. $\text{CaSi}_2$		238. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	
7.1	0.23	3.44 (10)	0.40	4.92	0.05	5.7	0.05	3.31	0.12	7.7	0.50
6.5	0.23	3.11	0.08	4.00	0.15	3.42	0.15	3.08	0.12	4.29	1.00
5.8	0.11	2.79 (25)	1.00	3.45	0.20	3.23	(40) 1.00	2.66	(25) 0.40	3.81	0.15
4.35	0.23	2.62	0.08	3.10	0.20	2.80	(30) 0.75	2.55	(17.5) 0.28	3.06	(25) 0.63
3.63	(17.5) 1.00	2.27	0.16	2.82	(20) 1.00	2.45	0.10	2.13	(17.5) 0.16	2.87	(25) 0.63
3.50	(10) 0.57	2.13	0.04	2.73	(8) 0.40	1.98	(25) 0.63	1.92	(62.5) 1.00	2.68	0.50
3.19	0.46	2.06	0.04	2.62	(10) 0.50	1.83	0.08	1.64	0.16	2.48	0.20
3.04	0.57	1.94	(5) 0.20	2.27	0.16	1.69	0.03	1.55	0.12	2.22	0.20
2.96	0.17	1.84	0.20	2.16	0.05	1.61	0.08	1.465	0.03	2.07	0.50
2.80	0.11	1.71	0.16	2.05	0.05	1.54	0.03	1.432	0.06*	1.88	0.25
2.57	(15) 0.86	1.450	0.08	1.95	0.45	1.476	0.08	1.355	0.03	1.79	0.20
2.32	0.11	1.310	0.08	1.89	0.05	1.400	0.05	1.245	0.11	1.66	0.10
2.11	0.46	1.240	0.04	1.83	0.30	1.293	0.03	1.215	0.02	1.62	0.15
1.93	0.17	1.109	0.08	1.80	0.30	1.250	0.08	1.119	0.02	1.58	0.10
1.82	0.23			1.72	0.10	1.180	0.03	1.165	0.06	1.435	0.13
1.76	0.11			1.54	0.05	1.140	0.03	1.150	0.02	1.360	0.10
1.71	0.23			1.50	0.05	1.110	0.03	1.110	0.06	1.325	0.10
1.59	0.17			1.480	0.05	1.040	0.03	1.045	0.02	1.270	0.03
1.51	0.11			1.450	0.20			1.020	0.02	1.240	0.15
		223. Calcium Chlorohydrophosphate		1.315	0.05			0.991	0.02	1.200	0.10
		4.32 (17.5)	0.43	1.285	0.05			0.961	0.02	1.138	0.08
		3.25 (40)	1.00	1.110	0.05			0.920	0.03	1.083	0.05
		2.99	0.31			232. $\alpha\text{-Ca}_2\text{SiO}_4$		0.904	0.02	1.037	0.03
		2.84	0.25			5.6	0.08	0.881	0.02	0.997	0.05
		2.66 (15)	0.37			4.32	0.24				
		2.58	0.05			4.05	0.06				
220. $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}^*$		2.42	0.05	228. $\text{Ca}(\text{H}_2\text{PO}_2)_2$		3.80	0.24				
12.0 (15)	0.75	2.29	0.20	7.4 (25)	0.63	3.38	0.09			236. $\text{CaSO}_4$	
5.6	0.20	2.22	0.15	3.70	0.63	3.01	(30) 0.48			239. $\text{CaS}^*$	
4.95	0.40	2.12	0.05	3.48 (40)	1.00	2.89	0.09	3.89	0.03	2.84 (125)	1.00
3.88 (20)	1.00	2.01	0.05	3.25 (30)	0.75	2.74	(62.5) 1.00	3.49	(75) 1.00	2.00 (125)	1.00
3.69 (15)	0.75	1.92	0.02	3.01	0.23	2.60	0.06	3.11	0.03	1.63	0.50
3.36	0.30	1.86	0.05	2.75	0.31	2.51	0.09	2.85	(50) 0.67	1.419	0.16
3.18	0.40	1.74	0.07	2.60	0.25	2.44	0.06	2.46	0.07	1.268	(75) 0.60
2.96	0.63	1.66	0.02	2.26	0.15	2.32	0.06	2.32	(25) 0.33	1.158	0.32
2.81	0.20	1.51	0.02	2.20	0.10	2.24	0.05	2.26	0.01	1.004	0.06
2.65	0.75	1.465	0.05	2.05	0.08	2.18	0.06	2.20	0.33	0.946	0.14
2.56	0.50	1.192	0.02	2.02	0.13	2.02	0.06	2.08	0.11	0.897	0.08
2.44	0.40			1.86	0.25	1.90	(30) 0.48	1.99	0.11	0.856	0.06
2.14	0.30			1.76	0.13	1.80	0.32	1.93	0.04	0.788	0.05
2.07	0.20			1.71	0.10	1.75	0.20	1.86	0.27	0.759	0.08
2.00	0.40			1.60	0.03	1.68	0.20	1.74	0.20	0.689	0.03
1.93	0.75			1.50	0.05	1.63	0.28	1.64	0.27	0.670	0.02
1.84	0.05			1.375	0.03	1.53	0.08	1.59	0.03		
1.78	0.30	224. $\text{CaO}_2 \cdot \text{PO} \cdot \text{OC}_3\text{H}_5(\text{OH})_2$		1.225	0.03	1.495	0.06	1.56	0.05		
1.74	0.15	14.2 (100)	1.00	1.180	0.03	1.470	0.09	1.52	0.07		
1.70	0.20	7.0	0.03			1.440	0.05	1.487	0.08	240. $\text{CaSO}_3$	
1.65	0.20	5.2 (7)	0.07			1.405	0.05	1.420	0.08	5.5 (10)	0.40
1.60	0.15	3.48 (7)	0.07			1.300	0.03	1.395	0.07	4.85	0.08
1.57	0.10	3.10	0.01			1.268	0.03	1.360	0.01	4.32	0.08
1.53	0.20	2.21	0.01	229. $\text{Ca}(\text{NaHPO}_2)_2$		1.254	0.09	1.318	0.09	3.80	0.32
1.460	0.15	2.05	0.02	7.0 (20)	0.67	1.230	0.05	1.296	0.03	3.16 (25)	1.00
1.405	0.25	1.81	0.01	5.7	0.10	1.180	0.02	1.275	0.09	2.82	0.24
1.365	0.10	1.73	0.02	4.90	0.20	1.160	0.09	1.215	0.05	2.62	(15) 0.60
1.333	0.15			4.00	(20) 0.67	1.134	0.09	1.197	0.01	2.45	0.16
1.266	0.15			3.48	0.07	1.092	0.06	1.163	0.07	2.22	0.16
1.230	0.20			3.24	(30) 0.17	1.075	0.02	1.103	0.09	2.12	0.16
		225. Calcium Lactophosphate		3.09	1.00	1.013	0.03			2.06	0.16
		10.0 (8)	0.89	2.95	0.03	0.957	0.03			1.95	0.36
221. $\text{Ca}_3(\text{PO}_4)_2$		8.9 (9)	1.00	2.86	0.03					1.85	0.40
6.6	0.10	7.7	0.44	2.71	0.03					1.81	0.32
5.2	0.15	4.30	0.22	2.60	0.23					1.67	0.28
4.11	0.10	4.04	(6) 0.67	2.44	0.07	233. $\beta\text{-Ca}_2\text{SiO}_4$		6.0	0.40	1.62	0.24
3.47	0.20	3.28	0.11	2.30	0.17	2.77 (25)	1.00	3.48	0.30	1.52	0.24
3.22	(25) 0.63	3.09	0.33	2.12	0.07	2.62 (10)	0.40	3.00 (30)	0.60	1.480	0.12
2.89	(40) 1.00	2.95	0.22	1.99	0.03	2.43	0.16	2.80 (50)	1.00	1.440	0.08
2.78	0.15	2.62	0.33	1.91	0.20	2.28	0.12	2.34	0.02	1.410	0.04
2.62	(30) 0.75	2.45	0.22	1.87	0.03	2.19	(12.5) 0.50	2.13	0.18	1.350	0.08
2.54	0.10	2.28	0.11	1.81	0.03	2.03	0.16	1.85	(30) 0.60	1.320	0.04
2.42	0.15	2.18	0.22	1.78	0.03	1.98	0.32	1.74	0.02	1.280	0.04
2.27	0.20	2.01	0.11	1.69	0.03	1.90	0.16	1.69	0.10	1.245	0.08
2.20	0.15	1.88	0.11	1.62	0.03	1.80	0.12	1.53	0.04	1.222	0.08
2.09	0.15			1.57	0.03	1.70	0.08	1.470	0.02	1.112	0.08
2.02	0.15			1.51	0.03	1.62	0.16	1.445	0.02		
1.94	0.31			1.450	0.03	1.52	0.12	1.350	0.02		
1.90	0.25			1.328	0.03	1.485	0.12	1.300	0.08		
1.83	0.15					1.370	0.08	1.262	0.04		
1.79	0.15					1.290	0.04	1.243	0.04		
1.74	0.50	4.92	0.16			1.250	0.04	1.210	0.02		
1.69	0.10	3.80	0.16			1.180	0.04	1.150	0.04		
1.64	0.08	3.31 (12.5)	1.00	230. $\text{Ca}(\text{C}_6\text{H}_5\text{OHCOO})_2 \cdot 3\text{H}_2\text{O}$		1.125	0.04	1.125	0.02		
1.61	0.10	3.20	0.48	9.9 (40)	1.00			1.070	0.02	7.2 (8)	0.40
1.56	0.22	3.03 (8)	0.64	6.0 (20)	0.50			1.038	0.02	6.7 (8)	0.40
1.470	0.05	2.78 (12.5)	1.00	5.0	0.31			1.012	0.02	5.3	0.20
1.420	0.07	2.65	0.16					1.000	0.02	4.85	0.20
1.390	0.05	2.56	0.16					0.958	0.02	4.18	0.10
1.315	0.03	2.33	0.24					0.920	0.02	3.30	0.15
1.260	0.10	2.22	0.24							3.05	0.40
1.225	0.05	2.10	0.56							2.80	0.10
1.190	0.05	1.98	0.64							2.68	0.05
1.155	0.05	1.95	0.16							2.55 (20)	1.00
1.128	0.15	1.89	0.08							2.34	0.05
1.102	0.05	1.83	0.48							2.24	0.15
1.063	0.03	1.77	0.40							2.07	0.20
1.038	0.07	1.72	0.08							1.95	0.10
1.018	0.05	1.68	0.08							1.87	0.15
		1.62	0.40							1.78	0.10
		1.57	0.16								
		1.53	0.16								
		1.495	0.16								
		1.458	0.16								
		1.420	0.08								
		1.390	0.08								
		1.332	0.24								
		1.300	0.16								
		1.229	0.16								
		1.200	0.08								



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>
242. $\text{Ca}(\text{CNS})_2 \cdot 3\text{H}_2\text{O}$		247. $\text{CH}_3\text{CONH}_2$		252. $\text{C}_6\text{H}_5\text{COOH}$		257. $\text{C}_6\text{H}_5\text{CH}:\text{CHCOOH}$		263. $(\text{C}_6\text{H}_5)_2\text{O}$		268. $\text{CH}_2\text{OHCOOH}$	
6.1	0.08	6.4	0.03	11.0	0.20	9.0	0.16	10.0	0.25	6.5	0.16
4.86	0.08	5.7	0.63	5.5	0.25	5.9	0.16	4.59	1.00	4.44	0.20
4.41	(20)	4.22	0.03	5.2	(40)	4.82	(25)	3.78	(30)	4.20	0.16
4.20	(20)	4.02	0.03	4.66	(40)	4.29	1.00	3.55	(40)	4.09	(15)
3.93	0.17	3.56	1.00	4.20	(50)	4.11	0.08	3.16	1.00	3.80	0.02
3.34	0.05	3.30	0.10	3.75	(40)	3.89	0.50	2.92	0.05	3.52	(50)
3.05	(75)	3.20	0.10	3.45	(50)	3.50	(17.5)	2.48	0.05	3.35	0.08
2.69	0.04	2.87	0.18	3.21	0.60	3.30	0.70	2.33	0.13	3.20	0.02
2.60	0.03	2.52	0.08	2.98	0.50	3.17	0.04	2.25	0.05	2.94	0.08
2.46	0.11	2.33	0.08	2.74	0.12	3.02	(20)	2.19	0.03	2.80	0.12
2.38	0.07	2.17	0.08	2.58	0.02	2.63	0.08	1.92	0.08	2.71	0.02
2.28	0.05	2.00	0.03	2.50	0.12	2.23	0.12	1.86	0.05	2.63	0.14
2.20	0.03	1.86	0.03	2.42	0.20	2.16	0.04	1.81	0.10	2.47	(20)
2.13	0.09	1.81	0.03	2.32	0.08			1.70	0.03	2.27	0.12
2.06	0.08	1.76	0.05	2.21	0.10					2.19	0.04
1.95	0.09	1.72	0.05	2.10	0.04					2.11	0.04
1.91	0.09	1.59	0.03	2.02	0.06					2.03	0.10
1.79	0.01			1.92	0.02					1.95	0.02
1.73	0.01			1.87	0.02					1.89	0.04
1.70	0.01			1.81	0.04					1.70	0.06
1.66	0.05			1.72	0.08						
1.60	0.09			1.67	0.04						
1.55	0.03			1.61	0.06						
1.52	0.01			1.55	0.04						
1.462	0.03										
1.412	0.03										
1.379	0.04										
1.345	0.01										
1.295	0.01										
1.263	0.03										
243. $\text{CaWO}_4^*$		248. $\text{CH}_3\text{CONHC}_6\text{H}_5$		253. $(\text{C}_6\text{H}_5)_2\text{CO}$		258. $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$		264. $(\text{C}_6\text{H}_5)_2\text{SO}$		269. $(\text{CH}_2)_5\text{N}_4$	
4.76	(12.5)	10.0	0.89	6.3	0.16	6.4	0.25	6.7	0.20	7.0	(4)
3.09	(40)	8.6	0.22	5.6	0.72	5.4	0.08	6.1	0.20	5.9	(4)
2.83		8.0	0.22	4.80	1.00	4.94	(40)	5.4	1.00	4.97	(30)
2.61		7.5	0.22	4.38	(12.5)	4.57	0.43	4.12	(20)	4.00	0.13
2.28		6.8	0.56	4.03	(10)	4.10	0.10	3.85	(7)	3.85	0.13
1.98		5.8	0.89	3.78	0.80	3.73	0.31	3.48		3.73	0.13
1.92	(9)	5.2	0.33	3.59	0.32	3.42	(40)	3.25		3.25	0.16
1.85		4.77	0.22	3.17	0.48	3.10	0.25	2.98		3.22	0.13
1.67		4.45	0.67	3.05	0.08	2.86	(30)	2.69		2.86	0.10
1.62		4.02	1.00	2.92	0.16	2.66		2.32		2.75	0.13
1.58		3.75	0.89	2.80	0.16	2.55		2.01		2.65	0.10
1.54		3.45	0.67	2.76	0.16	2.48		1.92		2.49	0.10
1.243		3.21	0.11	2.72	0.08	2.42		1.82		2.33	0.10
1.200		3.04	0.67	2.60	0.08	2.30				2.02	0.10
1.165		2.81	0.11	2.48	0.08	2.20				1.88	0.07
1.080		2.56	0.11	2.39	0.08	2.09				1.78	0.03
1.010		2.36	0.22	2.17	0.08	1.77				1.72	0.03
244. $\text{CaC}_2\text{H}_2\text{O}_2\text{N}_4$		2.27	0.11	2.04	0.08					1.37	0.03
9.9		2.13	0.11	1.92	0.08						
8.3											
7.0											
6.0											
5.5											
4.85	(7)										
4.45											
4.00											
3.61											
3.25	(30)										
3.05											
2.88											
2.72	(7)										
2.48											
2.40											
2.31											
2.21											
2.08											
1.94											
1.83											
1.62											
245. $\text{C}^*$											
3.38	(100)										
2.12											
2.02	(10)										
1.69											
1.227	(17.5)										
1.150											
1.120											
1.049											
0.991											
0.828											
0.796											
0.707											
0.695											
246. $\text{CH}_3\text{CH}(\text{NH}_2)\text{OH}$											
8.5	(15)										
6.2	(25)										
5.7											
4.22											
3.98											
3.70	(17.5)										
3.29											
3.10											
2.81											
2.67											
2.59											
2.42											
2.32											
2.24											
2.16											
2.08											
1.99											
250. $\text{C}_{11}\text{H}_{12}\text{ON}_2$											
7.7											
6.7	(17.5)										
5.8											
4.49	(25)										
4.18	(12.5)										
3.77											
3.12											
2.95											
2.77											
2.65											
2.30											
2.25											
2.12											
1.90											
1.227	(17.5)										
1.150											
1.120											
1.049											
0.991											
0.828											
0.796											
0.707											
0.695											
251. $\text{C}_6\text{H}_5\text{CO}_2\text{HCO}_2\text{CH}_3$											
11.7											
5.7	(25)										
4.29											
3.92	(8)										
3.30	(10)										
2.84											
2.73											
2.60											
2.47											
2.39											
2.32											
2.15											
2.06											
1.87											
1.80											
252. $\text{C}_6\text{H}_5\text{COOH}$											
11.0											
5.5											
5.2	(40)										
4.66											
4.20											
3.75	(40)										
3.45	(50)										
3.21											
2.98											
2.74											
2.58											
2.50											
2.42											
2.32											
2.21											
2.10											
2.02											
1.92											
1.87											
1.81											
1.72											



(Starred patterns were checked with published crystal structure data)

(starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>
272. C <sub>6</sub> H <sub>4</sub> IOH		277. C <sub>10</sub> H <sub>7</sub> OH		282. (COOH) <sub>2</sub> .2H <sub>2</sub> O		287. C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>		292. C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> .CH <sub>2</sub> CN		297. Ce(NO <sub>3</sub> ) <sub>3</sub> .6H <sub>2</sub> O	
9.8	0.33	5.9	(20) 0.80	6.0	0.20	7.6	(8) 0.53	7.5	(20) 0.80	11.5	0.24
7.2	0.66	4.40	0.20	4.75	0.20	6.9	0.53	5.5	0.08	10.0	0.16
6.5	0.17	3.66	(25) 1.00	3.95	0.07	6.0	0.07	4.30	0.08	8.7	0.16
5.7	0.20	3.21	(7) 0.28	3.45	0.09	5.7	0.33	3.88	0.24	8.1	0.64
5.1	0.83	2.95	0.16	3.08	(75) 1.00	5.4	0.13	3.60	(25) 1.00	6.8	0.80
4.86	0.27	2.70	0.16	2.87	0.13	4.71	(12.5) 0.83	3.35	0.32	6.3	1.00
4.60	0.27	2.19	0.04	2.60	0.08	4.50	0.47	3.15	(12.5) 0.50	5.8	0.64
4.27	0.13	2.11	0.04	2.41	(25) 0.33	4.30	0.40	3.00	0.04	5.4	0.80
3.97	0.42	2.02	0.04	2.27	(25) 0.33	4.00	0.53	2.81	0.08	5.2	0.48
3.79	0.66	1.94	0.12	2.17	0.01	3.79	0.27	2.68	0.08	4.70	1.00
3.60	0.40	1.75	0.04	1.98	0.05	3.59	(15) 1.00	2.51	0.04	4.39	(12.5) 1.00
3.38	0.27			1.93	0.03	3.37	0.07	2.32	0.04	3.97	0.80
3.22	1.00			1.83	0.05	3.22	0.13	2.17	0.08	3.80	0.48
3.05	0.27			1.77	0.01	3.10	0.13	2.08	0.08	3.64	0.32
2.97	0.66	278. C <sub>10</sub> H <sub>6</sub> OH.SO <sub>3</sub> H		1.72	0.03	2.88	0.47	1.95	0.04	3.35	0.64
2.79	0.17	14.0	0.07	1.58	0.01	2.80	0.13	1.88	0.04	3.25	0.64
2.70	0.17	5.3	0.07	1.54	0.07	2.67	0.07	1.79	0.04	3.00	0.32
2.57	0.10	4.55	(15) 1.00	1.486	0.01	2.58	0.13			2.91	0.64
2.41	0.27	3.67	(6) 0.40	1.433	0.01	2.49	0.13			2.84	0.64
2.25	0.20	3.44	0.27			2.41	0.13			2.62	0.80
2.17	0.13	3.09	(8) 0.53			2.34	0.33	293. C <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> C:(SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		2.53	0.48
2.13	0.42	2.77	0.13	283. C <sub>6</sub> HCl <sub>5</sub>		2.24	0.33	6.6	(50) 1.00	2.45	0.40
1.98	0.20	2.65	0.13			2.18	0.13	5.4	(10) 0.20	2.41	0.32
1.93	0.20	2.44	0.08	8.4	0.27	2.06	0.27	4.98	0.10	2.30	0.40
1.88	0.23	2.25	0.07	7.1	0.33	1.95	0.07	4.65	0.16	2.25	0.40
1.81	0.10	2.18	0.07	6.6	(10) 0.67	1.90	0.13	4.38	0.04	2.19	0.32
1.69	0.10	2.00	0.07	5.2	0.07	1.80	0.13	4.15	(10) 0.20	2.11	0.64
		1.88	0.20	4.00	0.40	1.74	0.07	3.78	0.12	2.03	0.24
		1.455	0.07	3.60	0.67	1.69	0.20	3.60	0.12	2.00	0.16
273. C <sub>6</sub> H <sub>4</sub> CO.CO.H:N				3.34	1.00	1.64	0.07	3.27	0.08	1.95	0.48
6.5	0.13	279. N(CH <sub>2</sub> COOH) <sub>3</sub>		3.10	(12.5) 0.83			2.94	0.12	1.86	0.32
5.7	0.50	6.0	0.08	2.87	0.40			2.80	0.04		
5.2	0.10	4.48	0.08	2.79	0.53	288. (CH <sub>3</sub> ) <sub>2</sub> C(SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		2.68	0.06	298. Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> .9H <sub>2</sub> O	
4.66	0.03	3.69	(25) 1.00	2.60	0.27	(CH <sub>3</sub> ) <sub>2</sub> C(SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		2.57	0.10	5.4	(12.5) 1.00
3.49	(20) 0.66	3.47	0.12	2.53	0.27	6.7	(25) 1.00	2.35	0.06	4.89	(7) 0.56
3.21	(30) 1.00	3.15	(17.5) 0.08	2.01	0.13	6.0	(10) 0.40	2.31	0.02	4.32	0.24
2.86	0.03	2.99	(10) 0.70	1.91	0.07	5.3	0.32	2.17	0.02	3.20	(6) 0.48
2.60	0.03	2.65	0.40	1.84	0.27	4.9	(10) 0.40	2.08	0.06	2.90	0.32
2.14	0.03	2.58	0.16	1.75	0.07	4.54	0.32			2.67	0.24
2.06	0.03	2.58	0.08	1.65	0.13	4.29	0.32			2.10	0.48
1.74	0.03	2.44	0.08	1.58	0.07	4.06	0.24	294. NH <sub>2</sub> .CO.NH <sub>2</sub>		1.95	0.48
1.60	0.03	2.32	0.32	1.490	0.07	3.60	0.24	4.00	(75) 1.00	1.66	0.08
1.470	0.03	2.22	0.12			2.92	0.28	3.61	(30) 0.40	1.59	0.16
		2.11	0.24	284. <i>o</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> OH		2.69	0.16	3.04	(40) 0.53	1.490	0.08
		1.99	0.28	6.0	0.06	2.51	0.08	2.82	0.11	1.450	0.08
		1.97	0.08	5.2	0.71	2.42	0.08	2.52	0.20		
274. C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> .H <sub>2</sub> O		1.83	0.08	(12.5) 0.71	0.06	2.34	0.04	2.41	0.20		
7.1	0.20	1.77	0.08	(17.5) 1.00	0.06	2.14	0.08	2.34	0.03		
5.4	0.35	1.58	0.08	(10) 0.57	0.04	2.02	0.12	2.23	0.08	299. CeO <sub>2</sub> *	
4.51	(20) 1.00	1.50	0.04	3.40	0.34	1.98	0.04	2.17	0.20	3.11	(50) 1.00
4.20	(6) 0.30	1.445	0.04	3.17	0.29	1.89	0.04	2.08	0.01	2.69	0.25
3.91	0.10	1.410	0.04	2.87	0.29	1.77	0.04	2.01	0.08	1.90	(40) 0.80
3.73	0.25			2.42	0.23			1.84	0.13	1.62	(30) 0.60
3.50	0.15	280. NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> .NH <sub>2</sub>		2.12	0.06	289. C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> .H <sub>2</sub> O		1.75	0.01	1.55	0.10
3.22	0.10	7.1	0.07	1.84	0.06	7.7	0.10	1.67	0.13	1.347	0.10
2.87	0.10	5.4	0.23	1.76	0.06	4.76	0.20	1.51	0.08	1.237	0.25
2.70	0.10	4.95	0.23			4.34	(30) 1.00	1.368	0.03	1.207	0.16
2.59	0.15	4.58	(17.5) 0.58	285. <i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> OH		4.00	0.13	1.329	0.07	1.101	0.20
2.37	0.15	3.80	0.50	4.55	(25) 1.00	3.57	0.27	1.259	0.01	1.037	0.18
2.12	0.10	3.48	(30) 1.00	4.25	(20) 0.80	3.04	(17.5) 0.58	1.230	0.01	0.954	0.04
1.90	0.05	3.13	(17.5) 0.58	3.88	(25) 1.00	2.81	0.42	1.177	0.04	0.912	0.14
		3.01	0.27	3.15	0.80	2.70	0.03			0.899	0.02
275. C <sub>2</sub> H <sub>2</sub> (COOH) <sub>2</sub>		2.90	0.13	3.00	0.04	2.52	(17.5) 0.58			0.853	0.04
5.3	0.10	2.74	0.07	2.39	0.12	2.44	0.27	295. Ce		0.816	0.02B
5.0	(15) 0.38	2.62	0.07	2.23	0.04	2.32	0.13	3.20	(12.5) 1.00	0.756	0.04
3.97	(15) 0.38	2.58	0.07	2.17	0.04	2.14	0.10	2.96	0.16	0.722	0.04
3.18	(40) 1.00	2.40	0.03	1.89	0.04	2.02	0.03	2.81	(9) 0.72	0.703	0.02
2.98	0.03	2.03	0.03	1.82	0.04	1.93	0.13	2.47	0.16		
2.77	0.20	1.96	0.03	1.66	0.04	1.77	0.03	2.25	0.16		
2.66	0.15	1.86	0.03	1.58	0.04	1.68	0.06	1.96	0.24	300. Ce(SO <sub>4</sub> ) <sub>2</sub> .4H <sub>2</sub> O	
2.47	0.03	1.75	0.03					1.85	(5) 0.40	6.8	0.13
2.35	0.25	1.70	0.03					1.68	0.16	5.8	0.05
2.27	0.08			286. C <sub>6</sub> H <sub>5</sub> OHCOOH				1.57	0.08	5.4	0.03
2.22	0.15	281. NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO		4.65	(10) 0.66	4.58	0.66			4.65	(30) 1.00
2.00	0.03	6.2	(12.5) 0.63	4.50	0.53	4.50	0.53			4.41	0.13
1.95	0.05	4.74	(12.5) 0.63	3.65	0.66	3.65	0.66	296. CeCl <sub>3</sub>		3.96	0.07
1.91	0.05	4.22	0.63	3.34	0.27	3.34	0.27	8.6	0.12	3.69	0.07
1.77	0.03	3.69	0.10	3.18	0.53	3.18	0.53	7.9	0.08	3.45	(5) 0.17
1.73	0.03	3.53	0.30	2.90	0.42	2.90	0.42	6.8	(50) 1.00	3.33	0.03
1.68	0.03	3.35	0.25	2.81	0.66	2.81	0.66	5.7	(15) 0.06	3.22	(10) 0.33
1.58	0.03	3.18	(20) 1.00	2.58	0.83	2.58	0.83	5.3	0.30	2.98	0.07
1.480	0.03	3.05	0.05	2.43	0.66	2.43	0.66	5.0	0.12	2.91	0.03
		2.88	0.10	2.25	0.13	2.25	0.13	4.50	0.16	2.82	0.10
276. C <sub>10</sub> H <sub>8</sub>		2.70	0.10	2.08	0.13	2.08	0.13	4.30	0.30	2.70	0.13
11.5	0.07	2.53	0.05	1.97	0.02	1.97	0.13	3.99	0.25	2.60	0.07
9.9	0.13	2.38	0.05	1.74	0.06	1.74	0.13	3.82	0.30	2.48	0.03
8.7	0.13	2.23	0.05	1.67	0.06	1.67	0.13	3.31	0.20	2.39	0.03
7.9	0.20	2.15	0.05	1.57	0.08	1.57	0.13	3.17	0.12	2.33	0.03
7.2	0.20	2.04	0.10	1.51	0.03	1.51	0.13	3.07	0.02	2.23	0.03
4.52	(15) 1.00	1.58	0.05	1.460	0.02	1.460	0.20	2.83	0.12	2.10	0.10
4.10	(8) 0.53				0.06		0.27	2.63	0.16	2.05	0.07
3.49	0.27				0.03			2.53	0.04	2.00	0.10
3.37	(10) 0.67							2.48	0.16	1.88	0.03
3.00	0.40							2.38	0.10	1.83	0.07
2.75	0.07			291. CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NH <sub>2</sub>		8.2	(3) 0.60	2.30	0.08	1.76	0.05
2.42	0.20			6.2	0.60	6.2	0.60	2.21	0.30	1.67	0.05
1.91	0.07			5.7	0.40	5.7	0.40	2.08	0.02	1.62	0.05
1.84	0.07										



(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
301. Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		305. CsI*		311. CrBr <sub>3</sub> ·6H <sub>2</sub> O		315. Cr <sub>2</sub> O <sub>3</sub> *		19. CrK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O*		324. CoCO <sub>3</sub> *	
9.5	0.06	3.22 (40)	1.00	6.2 (2)	1.00	3.62	0.45	7.0	0.12	3.64 (7)	0.40
8.0	0.02	2.27 (6)	0.15	5.5 (2)	1.00	2.67	(40) 0.70	5.5	0.16	2.76 (17.5)	1.00
6.7	0.04	1.86 (15)	0.38	5.3	0.75	2.47	(40) 0.70	4.98	0.08	2.34	0.11
6.1	0.50	1.61	0.10	4.90	0.50	2.17	0.30	4.31	1.00	2.12	0.11
5.5	(50)	1.435	0.13	4.49	0.50	2.03	0.45	4.08	0.30	1.96	0.11
4.85	0.04	1.218	0.10	4.15	0.50	1.81	(50) 1.00	3.68	(30) 0.60	1.71 (12.5)	0.71
4.33	0.16	1.074	0.04	3.92	0.75	1.67	0.06	3.26 (17.5)	0.35	1.50	0.11
3.50	0.50			3.52 (2)	1.00	1.58	0.30	3.04	0.30	1.415	0.11
3.03	0.80			3.42	1.00	1.465	0.45	2.87	0.02	1.355	0.06
2.85	(50)	1.00		3.30	1.00	1.432	0.16	2.81	0.12		
2.71	0.04			3.12	0.75	1.294	0.06	2.72	0.12		
2.60	0.02	4.07 (40)	0.53	2.96	0.75	1.236	0.06	2.59	0.06	325. Cobaltous Chloride	
2.47	0.14	3.16 (75)	1.00	2.82	0.50	1.209	0.06	2.48	0.12	5.8 (50)	1.00
2.37	0.14	2.66	0.40	2.66	1.00	1.172	0.05	2.34	0.06	4.31	0.06
2.27	0.14	2.50	0.20	2.57	0.50	1.148	0.06	2.25	0.06	3.04	0.04
2.15	0.35	2.03	0.27	2.51	0.50	1.123	0.06	2.15	0.04	2.84	0.02
2.08	0.04	1.96	0.20	2.44	0.75	1.087	0.12	2.03	0.12	2.71	0.06
2.01	0.08	1.82	0.20	2.36	0.50	1.041	0.10	1.97	0.06	2.48	0.06
1.93	0.06	1.71 (40)	0.53	2.21	0.50	1.025	0.02	1.93	0.16	2.38	0.04
1.87	0.60	1.58	0.13	2.15	0.50	0.946	0.06α <sub>1</sub>	1.85	0.04	2.30	0.04
1.82	0.02	1.472	0.13	2.08	0.50			1.74	0.04	2.23	0.02
1.76	0.12	1.357	0.20	1.97	1.00			1.69	0.08	2.14	0.02
1.71	0.20	1.331	0.07	1.94	1.00			1.63	0.10	2.07	0.03
1.68	0.12	1.250	0.08	1.91	0.50					1.98	0.02
1.63	0.04	1.225	0.08	1.88	0.50					1.92	0.02
1.56	0.14	1.191	0.11	1.80	0.50					1.86	0.02
1.495	0.04	1.161	0.07	1.75	0.75			320. Co*		1.77 (30)	0.60
1.463	0.04	1.115	0.04	1.69	0.50			(17.5)	0.44	1.70 (10)	0.20
1.430	0.04	1.051	0.07					(9)	0.22	1.64	0.02
1.370	0.04	1.030	0.05						0.22	1.59	0.02
1.320	0.20			312. CrF <sub>3</sub> ·4H <sub>2</sub> O					0.05	1.53	0.02
1.275	0.08			4.70 (75)	1.00				0.15	1.443	0.04
1.260	0.08			4.09 (50)	0.67				0.03	1.307	0.02
1.220	0.06			3.09	0.03				0.01	1.181	0.02
1.185	0.02			2.57 (50)	0.67				0.03	1.157	0.03
1.165	0.04			2.04	0.09				0.01	1.120	0.08
1.138	0.02			1.87	0.40				0.01	1.025	0.06
1.108	0.02			1.82	0.01				0.05	0.970	0.03
1.084	0.04			1.77	0.11				0.01		
1.052	0.04			1.73	0.11				0.03		
				1.67	0.01				0.05		
				1.63	0.17				0.02		
				1.56	0.01				0.06		
				1.53	0.03				0.02		
				1.490	0.03				0.02		
				1.460	0.08						
				1.423	0.01						
				1.395	0.03						
				1.360	0.07						
				1.300	0.03						



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>						
328. Co(NH <sub>3</sub> ) <sub>6</sub> Cl <sub>3</sub>		333. CoC <sub>2</sub> O <sub>4</sub>		338. CoSO <sub>4</sub>		343. CuAl <sub>2</sub> O <sub>4</sub> *		349. 2CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>		354. CuCl <sub>2</sub> ·2NH <sub>4</sub> Cl·2H <sub>2</sub> O							
6.7	0.05	4.73	(40)	1.00	4.82	(40)	0.64	2.85	(5)	0.33							
6.1	0.05	3.90		0.15	3.80		0.08	2.43	(15)	1.00	5.1	(12.5)	0.71	5.5	(30)	1.00	
5.7	(40)	1.00	3.60	(12.5)	0.31	3.40	(62.5)	1.00	2.01		0.27	3.68		0.23	4.00		0.23
5.2	0.10	2.95	(25)	0.50	3.30		0.16	1.85		0.07	3.51	(17.5)	1.00	3.39		0.07	
4.75	0.05	2.65		0.31	3.08	(30)	0.48	1.64		0.07	3.02		0.23	3.20		0.20	
4.08	0.20	2.55		0.15	2.57		0.16	1.55		0.20	2.51	(9)	0.51	3.12		0.20	
3.92	0.25	2.23		0.20	2.51		0.48	1.423	(10)	0.67	2.27		0.40	2.75	(15)	0.50	
3.50	(15)	0.38	2.16		0.03	2.40		0.02		0.07	2.09		0.06	2.68	(20)	0.66	
3.29		0.20	2.08		0.15	2.35		0.20			1.94		0.17	2.58		0.07	
3.08		0.13	2.02		0.15	2.20		0.24			1.82		0.17	2.51		0.03	
2.99		0.13	1.89		0.18	2.10		0.16			1.79		0.06	2.40		0.03	
2.80		0.18	1.78		0.20	2.05		0.10			1.59		0.17	2.23		0.13	
2.68		0.08	1.70		0.03	1.97		0.20			1.52		0.17	2.09		0.07	
2.58	(15)	0.38	1.64		0.10	1.90		0.11			1.470		0.06	2.04		0.07	
2.38		0.10	1.58		0.05	1.81		0.13	6.9	(7)	0.56		0.06	1.98		0.07	
2.16	0.03	1.54		0.05	1.74		0.03	4.51	(12.5)	1.00	1.380		0.06	1.90		0.13	
2.04	0.20	1.480		0.05	1.70		0.10	4.01		0.40	1.345		0.06	1.79		0.07	
1.97	0.20	1.430		0.05	1.67		0.24	3.50	(7)	0.56	1.295		0.06	1.72		0.07	
1.86	0.18	1.365		0.03	1.62		0.10	3.07		0.08				1.67		0.07	
1.79	0.05	1.335		0.03	1.59		0.13	2.84		0.24				1.60		0.13	
1.74	0.08	1.170		0.03	1.56		0.06	2.62		0.08				1.490		0.03	
1.71	0.08	1.115		0.03	1.53		0.05	2.45		0.08				1.375		0.03	
1.66	0.08				1.498		0.11	2.32		0.08				1.190		0.03	
1.62	0.18				1.448		0.08	2.15		0.16							
1.50	0.08				1.412		0.08	1.92		0.08							
1.433	0.08				1.360		0.03	1.86		0.08							
329. CoCrO <sub>4</sub>		334. CoO*		339. CoSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O		345. Copper-Beryllium Alloy (12% Be)		350. CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>		355. CuCl <sub>2</sub> ·2KCl·2H <sub>2</sub> O							
3.30	(2)	0.50	2.45	(50)	0.67			6.0		0.35				5.4	(30)	0.75	
3.10	(2)	0.50	2.12	(75)	1.00			5.1	(8)	0.40				3.95		0.15	
2.89		0.50	1.50	(75)	1.00			3.68	(10)	0.50				3.73		0.08	
2.62	(4)	1.00	1.281		0.40			2.86	(20)	1.00				3.31		0.10	
2.36		0.50	1.227		0.40			2.49		0.25				3.17		0.44	
2.04		0.25	1.060		0.10			2.31		0.05				3.07		0.25	
1.73		0.50	0.975		0.10			2.16		0.05				2.71	(30)	0.75	
1.65		0.25	0.951		0.30			2.04		0.05				2.64	(40)	1.00	
1.55		0.50	0.869		0.20			1.94		0.05				2.56		0.03	
330. Co(OH) <sub>2</sub>		335. CoCo <sub>2</sub> O <sub>4</sub> *		340. Cb*		346. Copper Borate (ic)		351. CuCl*		352. CuCl <sub>2</sub>							
4.40	(75)	1.00	4.68		0.08			3.12	(50)	1.00				1.86		0.15	
2.44		0.23	2.86		0.20			2.70		0.08				1.80		0.05	
2.31	(62.5)	0.83	2.43	(100)	1.00			1.91	(30)	0.60				1.76		0.05	
1.80	(30)	0.40	2.34		0.06			1.63	(15)	0.30				1.70		0.03	
1.50		0.08	2.02		0.13			1.353		0.06				1.64		0.03	
1.425		0.40	1.65	(25)	0.25			1.240		0.08				1.58		0.25	
1.367		0.27	1.56	(30)	0.30			1.104		0.06				1.54		0.05	
1.215		0.05	1.432		0.02			1.043		0.04				1.490		0.03	
1.196		0.01	1.235		0.01									1.460		0.03	
1.162		0.04	1.084		0.01									1.430		0.03	
1.120		0.04	1.055		0.02									1.360		0.08	
331. (Mn, Co)(Mn, Co) <sub>2</sub> O <sub>4</sub> ; 2Co:Mn*		336. Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O		341. Cu*		347. CuBr*		348. CuBr <sub>2</sub>		353. CuCl <sub>2</sub> ·2H <sub>2</sub> O*							
(Mn, Co)(Mn, Co) <sub>2</sub> O <sub>4</sub> ; 2Co:Mn*			8.0		0.20			6.2		0.35				5.1	(20)	0.05	
			6.7	(50)	1.00			3.62		0.30				5.4		0.20	
4.76		0.10	4.87		0.40			3.08	(20)	1.00				4.90	(20)	1.00	
2.91		0.30	4.51		0.14			2.49	(20)	0.05				3.62		0.45	
2.48	(100)	1.00	4.04		0.12			2.02		0.05				3.43		0.20	
2.37		0.07	3.81		0.30			1.96	(10)	0.50				2.70		0.45	
2.05		0.20	3.60		0.04			1.92		0.45				2.57	(20)	1.00	
1.68		0.10	3.19		0.40			1.79	(30)	0.67				2.14	(12.5)	0.62	
1.58	(40)	0.40	2.95	(30)	0.60			1.71	(15)	0.50				2.05		0.05	
1.452	(50)	0.50	2.69	(30)	0.60			1.420		0.07				1.94		0.10	
1.302		0.03	2.60		0.08			1.305		0.13				1.83		0.20	
1.256		0.08	2.50		0.20			1.160		0.13				1.63		0.15	
1.242		0.02	2.40		0.20			1.094		0.07				1.56		0.10	
1.190		0.02	2.30		0.20	2.33	(125)	1.00		0.03				1.480		0.20	
1.101		0.03	2.20		0.20	1.65	(25)	0.20		0.03				1.440		0.15	
1.073		0.13	2.17		0.20	1.34	(40)	0.32		0.03				1.380		0.05	
1.031		0.03	2.05		0.16	1.16		0.06						1.319		0.10	
0.951		0.04	2.00		0.04	1.041		0.10						1.281		0.10	
332. Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O		337. Cobalt Stannate (ous)		342. (CuOAs <sub>2</sub> O <sub>3</sub> ) <sub>3</sub> ·- Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>		354. Copper Ammonium Chromate (ic)		355. Copper Ammonium Chromate (ic)		356. CuCrO <sub>4</sub> ·2CuO·2H <sub>2</sub> O							
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O			1.92		0.20	0.950		0.01						1.062		0.05	
			1.88		0.14	0.879		0.06									
			1.80		0.08	0.775		0.02									
			1.76		0.16	0.736		0.01									
			1.66		0.30												
			1.57		0.14												
			1.53		0.02												
			1.51		0.04												
4.60	(40)	1.00	1.472		0.10	2.08	(75)	1.00						5.1	(20)	0.50	
3.88		0.20	1.409		0.06	1.81	(40)	0.53						4.20	(10)	0.25	
3.70		0.15	1.370		0.04	1.277	(25)	0.33						3.57	(40)	1.00	
3.50		0.13	1.330		0.14	1.089		0.33						3.35		0.15	
3.29	(30)	0.75	1.255		0.04	1.043		0.09						2.93		0.08	
3.16		0.18	1.230		0.04	0.905		0.03			</						



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>
358. CuCr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O		363. K <sub>2</sub> CuFe(CN) <sub>6</sub>		368. CuMg <sub>2</sub> * (C <sub>6</sub> H <sub>4</sub> OHHSO <sub>3</sub> ) <sub>2</sub> Cu·6H <sub>2</sub> O		374. Cu(C <sub>6</sub> H <sub>4</sub> OHCOO) <sub>2</sub> ·4H <sub>2</sub> O		378. CuSO <sub>4</sub> ·5H <sub>2</sub> O		381. CuSO <sub>4</sub> ·5H <sub>2</sub> O	
6.7	0.33	5.1	0.38	4.60	(20) 0.50	11.7	(17.5) 0.44	14.9	(10) 0.57	5.7	0.33
5.5	0.17	3.63	(40) 1.00	4.43	0.50	5.8	0.15	13.0	0.17	5.6	0.42
4.78	0.33	3.06	0.20	3.67	0.25	5.5	0.20	9.9	0.46	5.2	0.03
4.50	0.33	2.86	0.08	2.53	0.15	5.2	0.10	9.0	0.46	4.70	(30) 1.00
4.21	0.33	2.57	(30) 0.75	2.41	0.38	4.63	(40) 1.00	7.6	(15) 0.86	4.00	(17.5) 0.58
3.95	0.67	2.36	0.15	2.28	(40) 1.00	3.95	(9) 0.23	6.5	0.11	3.70	(15) 0.50
3.67	0.83	2.29	0.31	2.13	0.08	3.52	0.15	5.8	0.11	3.50	0.03
3.55	(6) 1.00	2.13	0.25	2.03	(40) 1.00	3.27	0.03	4.80	(17.5) 1.00	3.29	0.33
3.40	(6) 1.00	2.06	(25) 0.63	1.86	0.10	3.00	0.15	4.48	0.29	3.03	0.20
3.15	(6) 1.00	1.82	0.15	1.72	0.05	2.91	0.08	3.51	0.40	2.83	0.27
2.99	0.67	1.63	0.25	1.66	0.05	2.81	0.03	3.25	0.23	2.74	0.27
2.71	0.33	1.58	0.03	1.61	0.08	2.70	0.10	3.12	0.23	2.66	0.13
2.61	0.83	1.52	0.03	1.56	0.05	2.58	0.10	2.96	0.11	2.56	0.10
2.48	1.00	1.460	0.05	1.475	0.15	2.44	0.05	2.79	0.11	2.42	0.33
2.24	0.17	1.390	0.05	1.439	0.10	2.28	0.08	2.70	0.11	2.33	0.07
2.16	0.17	1.360	0.05	1.408	0.20	2.21	0.03	2.58	0.11	2.19	0.07
2.06	0.17	1.340	0.03	1.313	0.10	1.95	0.08	2.43	0.11	2.08	0.03
2.01	0.17	1.275	0.03	1.268	0.15	1.90	0.08	2.34	0.11	2.02	0.10
1.86	0.17	1.215	0.05	1.137		1.82	0.03	2.27	0.11	1.98	0.03
1.83	0.17	1.150	0.05			1.75	0.03	2.13	0.11	1.91	0.10
1.74	0.17					1.72	0.03	2.07	0.11	1.83	0.10
1.52	0.17					1.65	0.03	1.97	0.11	1.77	0.03
1.49	0.17					1.61	0.03			1.74	0.03
359. 2Cu <sub>2</sub> C <sub>8</sub> H <sub>5</sub> O <sub>7</sub> ·5H <sub>2</sub> O		364. CuF <sub>2</sub> ·2H <sub>2</sub> O		369. Cu <sub>2</sub> Mg*		375. Cupric Phosphate (Fused)		379. CuSO <sub>4</sub>		382. CuSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	
7.4	(12.5) 0.25	4.73	(50) 1.00	4.07	(12.5) 0.50	4.15	0.32	4.20	(40) 0.53	6.1	0.27
5.6	(50) 1.00	4.31	0.08	2.12	(25) 1.00	3.76	0.32	3.92	0.03	5.4	(9) 0.30
4.55	(12.5) 0.25	3.50	0.12	2.03	(17.5) 0.70	3.10	0.32	3.55	(40) 0.53	4.19	(30) 1.00
3.85	0.25	2.66	0.10	1.76	0.28	2.96	(25) 1.00	2.62	(75) 1.00	3.74	(17.5) 0.58
3.56	0.12	2.57	(30) 0.60	1.61	0.20	2.80	(17.5) 0.70	2.41	0.40	3.38	0.13
3.13	0.08	2.44	0.20	1.354	0.50	2.69	(15) 0.60	2.31	0.09	3.04	0.30
2.92	0.08	2.34	0.06	1.245	0.50	2.58	0.40	2.08	0.05	2.82	0.17
2.66	0.08	2.14	0.12	1.190	0.20	2.42	0.16	2.01	0.03	2.70	0.03
2.49	0.04	1.98	(20) 0.40	1.074	0.12	2.18	0.32	1.96	0.12	2.53	0.10
2.41	0.02	1.89	0.20	1.061	0.32	2.06	0.24	1.77	0.09	2.42	0.23
2.19	0.08	1.69	0.04	1.016	0.04	1.98	0.20	1.67	0.03	2.21	0.03
1.99	0.08	1.63	0.06	0.986	0.04	1.82	0.04	1.58	0.11	2.16	0.03
1.93	0.08	1.59	0.16	0.916	0.24	1.74	0.08	1.55	0.03	2.08	0.03
1.88	0.06	1.54	0.08			1.69	0.16	1.50	0.01	1.96	0.03
1.82	0.04	1.490	0.06			1.65	0.04	1.461	0.01	1.90	0.07
1.70	0.04	1.443	0.02			1.62	0.08	1.430	0.03	1.82	0.03
1.66	0.04	1.330	0.04			1.59	0.32	1.400	0.03	1.72	0.03
1.56	0.02	1.310	0.02			1.57	0.32	1.375	0.11	1.460	0.03
1.325	0.02	1.238	0.04			1.56	0.16	1.305	0.03	1.425	0.03
360. CuCN		365. (NH <sub>4</sub> ) <sub>2</sub> CuF <sub>4</sub> ·2H <sub>2</sub> O		370. Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O		376. Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O		380. CuSO <sub>4</sub> ·H <sub>2</sub> O		383. CuSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	
3.78	(20) 1.00	6.6	0.04	5.8	(17.5) 1.00	9.9	(20) 1.00	5.1	0.15	6.0	0.20
3.18	(17.5) 0.88	5.5	0.04	5.4	0.06	6.9	(5) 0.25	4.81	(25) 0.63	5.3	0.16
3.02	0.15	4.70	(25) 1.00	4.70	0.34	4.80	0.08	4.43	0.38	4.21	(17.5) 0.70
2.89	0.05	3.02	(9) 0.36	4.04	(12.5) 0.72	4.32	0.15	4.00	0.13	3.68	(25) 1.00
2.62	0.15	2.57	0.08	3.65	0.46	3.90	0.05	3.64	0.31	3.30	0.12
2.35	(8) 0.40	2.43	0.08	3.38	0.34	3.34	0.10	3.40	1.00	2.99	0.40
2.25	0.05	2.14	0.08	3.00	0.46	3.02	(17.5) 0.87	3.15	0.50	2.83	0.36
2.15	0.05	1.97	(4) 0.16	2.63	(12.5) 0.72	2.65	0.20	3.00	0.15	2.65	0.08
361. CuK <sub>3</sub> (CN) <sub>4</sub>		366. Cu(CHO <sub>2</sub> ) <sub>2</sub>		371. Cu <sub>2</sub> O*		372. CuO*		377. CuOH·CuPO <sub>4</sub> *		384. CuFeS <sub>2</sub> *	
7.4	(15) 0.24	4.90	(17.5) 1.00	3.00	0.03	2.51	(62.5) 1.00	5.8	0.40	3.03	(30) 1.00
4.22	0.20	4.60	(12.5) 0.71	2.45	(40) 1.00	2.31	(62.5) 1.00	4.81	(25) 1.00	2.62	(25) 0.07
3.45	0.09	4.29	0.46	2.12	(12.5) 0.31	1.85	(12.5) 0.20	3.71	(12.5) 0.50	1.86	(6) 0.20
3.13	(62.5) 1.00	3.60	0.11	1.51	(17.5) 0.44	1.70	0.08	2.91	(25) 1.00	1.59	0.03
2.75	0.16	3.39	0.11	1.283	0.31	1.57	0.08	2.63	(25) 1.00	1.323	0.03
2.51	0.09	2.84	0.17	1.228	0.05	1.408	0.20	2.55	0.12	1.206	0.07
2.22	(20) 0.32	2.61	(12.5) 0.71	1.065	0.03	1.370	0.20	2.41	0.16	1.077	0.03
2.00	0.06	2.44	0.11	0.977	0.05	1.298	0.05	2.30	0.16		
1.81	0.13	2.20	0.06	0.953	0.03	1.258	0.10	2.07	0.06		
1.69	0.02	2.12	0.06	0.869	0.03	1.159	0.05B	2.01	0.12		
1.57	0.05	2.02	0.11	0.819	0.03	1.086	0.03	1.92	0.20		
1.405	0.06	1.95	0.11			1.007	0.03	1.81	0.08		
1.375	0.02	1.81	0.06			0.978	0.03	1.67	0.12		
1.310	0.02	1.75	0.06			0.885	0.03	1.62	0.12		
1.283	0.05	1.64	0.06					1.59	0.16		
1.115	0.02	1.53	0.06					1.56	0.16		
1.050	0.02							1.480	0.16		
362. Cu <sub>2</sub> Fe(CN) <sub>6</sub> ·7H <sub>2</sub> O		367. CuI*		373. CuCo <sub>2</sub> O <sub>4</sub> *		374. Cu <sub>2</sub> (OH) <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O		375. Cu <sub>2</sub> (OH) <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O		376. Cu <sub>2</sub> (OH) <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	
10.1	0.03	3.49	(50) 1.00	4.65	0.15	11.7	(17.5) 0.44	14.9	(10) 0.57	5.7	0.33
7.1	0.03	3.01	0.06	2.85	0.25	5.8	0.15	13.0	0.17	5.6	0.42
5.8	0.05	2.14	(40) 0.80	2.43	(40) 1.00	5.5	0.20	9.9	0.46	5.2	0.03
5.0	(40) 1.00	1.82	(30) 0.60	2.31	0.20	5.2	0.10	9.0	0.46	4.70	(30) 1.00
3.55	(30) 0.75	1.51	0.12	2.11	0.05	4.63	(40) 1.00	7.6	(15) 0.86	4.00	(17.5) 0.58
3.02	0.03	1.386	0.20	1.64	0.10	3.95	(9) 0.23	6.5	0.11	3.70	(15) 0.50
2.50	(20) 0.50	1.350	0.04	1.55	(12.5) 0.31	3.52	0.15	5.8	0.11	3.50	0.03
2.23	0.25	1.233	0.25	1.421	(15) 0.38	3.27	0.03	4.80	(17.5) 1.00	3.29	0.33
2.04	0.20	1.162	0.12	1.361	0.03	3.00	0.15	4.48	0.29	3.03	0.20
1.76	0.15	1.070	0.02	1.227	0.08	2.91	0.08	3.51	0.40	2.83	0.27
1.67	0.08	1.020	0.08	1.160	0.03	2.81	0.03	3.25	0.23	2.74	0.27
1.58	0.10	0.956	0.06	1.076	0.03	2.70	0.10	3.12	0.23	2.66	0.13
1.50	0.03	0.847	0.02	1.047	0.08	2.58	0.10	2.96	0.11	2.56	0.10
1.450	0.03	0.809	0.02			2.44	0.05	2.79	0.11	2.42	0.33
1.385	0.05	0.787	0.02			2.28	0.08	2.70	0.11	2.33	0.07
1.335	0.05					2.21	0.03	2.58	0.11	2.19	0.07
1.212	0.03					1.95	0.08	2.43	0.11	2.08	0.03
1.180	0.03					1.90	0.08	2.34	0.11	2.02	0.10



(Starred patterns were checked with published crystal structure data)

(Scattered patterns were checked with published crystal structure data)

$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$
385. $\text{Cu}_2\text{SO}_4 \cdot \text{H}_2\text{O}$		389. $\text{Er}_2\text{O}_3^*$		395. $\text{InCl}_3$		399. $\text{Ir}^*$		404. $\text{Fe}_2\text{Al}_5$		407. $\text{FeCl}_3$					
4.65 (12.5) 0.50	4.31 0.07	5.8 (62.5) 1.00	2.20 (25) 1.00	4.90 0.11	5.9 (20) 0.32										
4.15 (12.5) 0.50	3.06 (30) 1.00	5.3 0.13	1.91 (12.5) 0.50	3.86 0.24	5.7 0.32										
3.03 0.50	2.64 0.27	5.0 0.20	1.352 0.28	3.20 0.40	5.1 0.05										
2.77 0.12	2.49 0.03	4.50 0.24	1.153 (9) 0.36	2.39 0.10	4.79 0.06										
2.49 (25) 1.00	2.25 0.03	4.01 0.24	1.104 0.08	2.11 (62.5) 1.00	4.50 0.03										
2.35 0.04	2.07 0.13	3.82 0.06	0.878 0.08	2.05 (62.5) 1.00	3.49 0.03										
2.25 0.16	1.87 (15) 0.50	3.58 0.32	0.857 0.08	1.94 0.10	3.09 0.03										
2.19 0.08	1.81 0.07	3.41 0.10	0.782 0.04	1.90 0.08	3.03 0.03										
2.03 0.04	1.71 0.07	3.00 (25) 0.40	0.737 0.04	1.84 0.03	2.90 0.03										
1.89 0.16	1.59 (12.5) 0.42	2.84 0.32	0.647 0.04	1.76 0.08	2.68 (62.5) 1.00										
1.78 0.12	1.52 0.07	2.68 0.10		1.70 0.02	2.52 0.02										
1.66 0.04	1.323 0.03	2.55 (30) 0.48		1.63 0.02	2.40 0.02										
1.62 0.04	1.220 0.07	2.44 0.10	400. $\text{IrCl}_3$	1.59 0.03	2.23 0.02										
1.58 0.16	1.185 0.03	2.32 0.24	(25) 1.00	1.55 0.02	2.08 (25) 0.40										
1.55 0.08	1.145 0.03	2.23 0.13		1.52 0.10	2.02 0.02										
1.52 0.16	1.087 0.07	2.10 0.03		1.475 0.16	1.96 0.03										
1.483 0.12		2.05 0.16		1.418 0.02	1.75 0.32										
1.205 0.08		2.00 0.13	(25) 1.00	1.390 0.10	1.67 0.06										
	390. $\text{GeO}_2^*$	1.92 0.10		1.350 0.02	1.63 0.16										
386. $\text{CuC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$	4.31 0.20	1.84 0.24		1.300 0.16	1.460 0.06										
7.6 (15) 0.60	3.41 (50) 1.00	1.76 0.08		1.272 0.32	1.340 0.05										
5.9 (25) 1.00	2.48 0.14	1.63 0.11	(25) 1.00	1.240 0.08	1.300 0.02										
4.60 0.50	2.35 (12.5) 0.25	1.59 0.03		1.212 0.16	1.190 0.03										
4.33 0.50	2.28 0.16	1.51 0.03		1.180 0.02	1.116 0.05										
4.10 0.50	2.15 0.20	1.475 0.03		1.145 0.02	1.080 0.02										
3.80 0.40	2.00 0.02	1.445 0.06		1.102 0.08	1.063 0.03										
3.54 (25) 1.00	1.87 (12.5) 0.25	1.390 0.06		1.090 0.32	1.009 0.02										
3.30 0.04	1.71 0.12	1.328 0.06		1.068 0.16	0.985 0.03										
3.06 0.16	1.62 0.02			1.031 0.20											
2.90 0.32	1.56 0.25	396. $\text{In}_2\text{O}_3^*$		1.018 0.08											
2.54 0.32	1.495 0.08			1.190 0.04											
2.43 0.40	1.445 0.04	4.12 0.14		1.150 0.04											
2.35 0.04	1.410 0.25	2.91 1.00	(175)	1.128 0.16											
2.22 0.04	1.386 0.08	2.70 0.03		1.092 0.28											
2.15 0.16	1.339 0.10	2.52 0.43		1.074 0.04											
2.03 0.08	1.301 0.02	2.38 0.10		1.027 0.04											
1.91 0.40	1.277 0.10	2.26 0.02		1.000 0.16											
1.85 0.12	1.248 0.02	2.15 0.10													
1.81 0.16	1.228 0.06	2.06 0.02													
1.65 0.24		1.98 0.17		401. $\text{Fe}^*$											
1.61 0.08	391. $\text{Au}^*$	1.84 0.04		2.01 (40) 1.00											
1.50 0.16	(75) 1.00	1.78 (125) 0.71		1.428 (6) 0.15											
1.450 0.12	(40) 0.53	1.73 0.03		1.166 (15) 0.38											
1.370 0.12	2.03 0.53	1.68 0.02		1.010 0.10											
1.300 0.08	1.439 0.33	1.63 0.10		0.904 0.08											
1.218 0.08	1.227 (30) 0.40	1.60 0.03		0.825 0.03											
	1.173 0.09	1.55 0.06		0.764 0.10											
	1.019 0.03	1.52 (100) 0.57		0.676 0.03											
387. $\text{CuCNS}$	0.935 0.09	1.490 0.07													
5.5 (40) 1.00	0.910 0.07	1.458 0.07		402. $\text{FeAl}$											
3.25 (40) 1.00	0.832 0.04	1.429 0.03													
3.10 0.03	0.784 0.04	1.401 0.02		2.89 (15) 0.12											
2.72 0.05		1.375 0.05		2.04 (125) 1.00											
2.59 0.25	392. $\text{AuCN}^*$	1.350 0.03		1.67 0.04											
1.92 (20) 0.50	(30) 0.60	1.281 0.04		1.445 0.08											
1.82 0.20	(50) 1.00	1.262 0.05		1.295 0.03											
1.75 0.03	(50) 1.00	1.241 0.05		1.180 (25) 0.20											
1.66 0.05	2.54 0.02	1.225 0.02		1.025 0.02											
1.57 0.08	1.92 0.40	1.205 0.03		0.915 0.02											
1.470 0.05	1.69 0.16	1.190 0.01		0.834 0.01											
1.360 0.05	1.61 0.12	1.175 0.03		0.776 0.02											
1.260 0.03	1.467 0.20	1.159 0.14													
1.110 0.03	1.410 0.16	1.130 0.09		403. $\text{FeAl}_3^*$											
	1.271 0.04														
	1.200 0.04	397. $\text{I}_2^*$		4.07 0.17											
388. $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$	1.165 0.04			3.68 0.11											
6.8 0.20	1.110 0.04	3.69 (25) 1.00		3.54 0.11											
6.6 0.20	1.086 0.04	3.09 (25) 1.00		3.34 0.07											
5.9 0.40	1.018 0.04	2.52 0.08		3.25 0.07											
5.4 0.40	0.961 0.04	2.44 0.18		2.26 0.08											
5.0 0.20		2.33 0.15		2.15 0.08											
4.86 0.20	393. $\text{AuK}(\text{CN})_2$	2.11 0.15		2.08 (62.5) 0.83											
4.50 0.20	(10) 1.00	2.02 0.20		2.02 (75) 1.00											
4.36 0.20	9.0 0.10	1.97 0.30		1.93 0.09											
3.94 (4) 0.80	6.1 0.10	1.81 0.10	(7)	1.80 0.03											
3.55 (5) 1.00	5.7 0.10	1.76 0.10		1.445 (15) 0.20											
3.39 (5) 1.00	4.52 (2) 0.20	1.71 0.20		1.395 0.05											
3.08 0.20	4.00 0.10	1.51 0.10		1.355 0.01											
2.84 0.40	3.67 0.10	1.460 0.08		1.287 0.05											
2.52 0.20	3.36 0.10	1.400 0.05		1.263 0.03											
2.39 0.40	3.10 1.00			1.250 0.05											
2.32 0.20	2.84 0.20	398. $\text{I}_2\text{O}_5$		1.225 0.07											
2.27 0.20	2.40 0.10			1.180 0.04											
2.11 0.20	2.27 0.10	4.03 0.15		1.169 0.05											
2.03 0.20	2.03 0.10	3.79 (20) 0.50		1.127 0.03											
1.91 0.20	1.81 0.10	3.40 (30) 0.75		1.089 0.04											
1.76 0.20	1.68 0.10	3.28 (40) 1.00		1.061 0.04											
1.66 0.20	1.56 0.10	3.18 0.15													
1.51 0.20		2.92 0.05													
1.446 0.20	394. $\text{In}^*$ </														



(Starred patterns were checked with published crystal structure data)

[illegible]



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$
434. $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$		437. $\text{FeSO}_4 \cdot 3\text{H}_2\text{O}$		440. $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}^*$		443. $\text{FeS}_2^*$		447. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2 \cdot \text{H}_2\text{O}$		451. $\text{PbCO}_3^*$	
10.2	0.20	6.9	0.38			3.12	0.27			4.40	0.06
9.2	0.10	5.5	(40) 1.00	7.1	(40) 0.80	2.70	(50) 0.75	13.0	(40) 1.00	4.24	0.04
7.1	0.10	4.49	(40) 1.00	5.5	0.50	2.42	(30) 0.45	3.38	(7) 0.18	3.56	(25) 1.00
6.8	(8) 0.80	3.99	(30) 0.75	5.0	0.25	2.21	0.35	3.05	(15) 0.38	3.47	0.12
4.75	(8) 0.80	3.60	0.03	4.37	(50) 1.00	1.91	0.45	2.88	0.15	3.05	0.16
4.41	0.50	3.40	0.50	4.12	0.60	1.63	(62.5) 1.00	2.73	0.08	2.57	0.08
4.16	0.30	3.24	0.50	3.73	(40) 0.80	1.56	0.15	2.60	0.08	2.47	(8) 0.32
4.00	0.20	2.97	0.75	3.30	0.80	1.50	0.17	2.48	0.05	2.19	0.04
3.53	(10) 1.00	2.75	0.20	3.09	0.40	1.450	0.25	2.24	0.03	2.07	(7) 0.28
3.35	0.50	2.58	0.38	2.75	0.14	1.240	0.10	2.07	0.05	1.99	0.06
3.20	0.60	2.43	0.38	2.62	0.06	1.210	0.15	1.95	0.04	1.96	0.06
3.11	0.20	2.36	0.38	2.52	0.14	1.180	0.10	1.88	0.03	1.91	0.20
3.02	0.10	2.27	0.38	2.37	0.16	1.153	0.05	1.81	0.03	1.83	0.24
2.88	0.10	2.18	0.03	2.26	0.06	1.105	0.12	1.77	0.03	1.79	0.04
2.77	0.10	2.11	0.08	2.15	0.04	1.041	0.25	1.69	0.08	1.74	0.04
2.67	0.20	2.04	0.03	2.06	0.20	1.005	0.03	1.65	0.05	1.62	0.06
2.33	0.10	1.97	0.38	2.00	0.04	0.987	0.02	1.53	0.05	1.58	0.06
2.28	0.10	1.89	0.20	1.95	0.35	0.957	0.10	1.485	0.04	1.55	0.04
2.20	0.10	1.80	0.18	1.82	0.04	0.903	0.03	1.443	0.05	1.50	0.04
2.15	0.10	1.76	0.08	1.72	0.20	0.878	0.02			1.469	0.04
2.03	0.10	1.72	0.10	1.65	0.18	0.855	0.02	448. $\text{Pb}_3(\text{SbO}_4)_2$		452. $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	
1.94	0.10	1.67	0.10	1.61	0.12			5.8	(3) 0.30		
1.88	0.20	1.63	0.08	1.497	0.12	444. $\text{FeC}_4\text{H}_4\text{O}_6$		4.55	0.10		
1.82	0.10	1.59	0.03	1.455	0.08	7.3	0.15	4.35	0.10	4.45	0.33
1.77	0.20	1.57	0.03	1.425	0.10	5.8	(15) 0.75	3.88	0.10	4.24	0.33
1.68	0.10	1.55	0.03	1.376	0.08	4.64	0.40	3.48	(10) 1.00	3.61	(5) 0.83
1.63	0.10	1.51	0.10	1.337	0.02	4.44	(20) 1.00	3.20	0.10	3.28	(6) 1.00
1.60	0.10	1.488	0.03	1.310	0.04	3.63	0.75	3.00	0.20	2.62	(6) 1.00
1.55	0.10	1.452	0.18	441. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$		3.51	(17.5) 0.88	2.82	0.10	2.23	0.25
1.50	0.10	1.398	0.10			3.29	0.15	2.65	(4) 0.40	2.11	0.25
1.460	0.10	1.370	0.10	6.2	0.20	3.09	0.10	2.08	0.20	2.03	0.17
1.422	0.10	1.288	0.15	6.0	0.20	2.64	0.25	1.87	0.30	1.86	0.25
1.390	0.10	1.230	0.03	5.4	0.50	2.56	0.40	1.82	0.10	1.69	0.17
1.353	0.10	1.201	0.05	5.12	0.20	2.43	0.75	1.64	0.20		
435. $\text{FeSO}_4$			0.03	4.46	0.20	2.27	0.10	1.55	0.10	453. $\text{PbCl}_2^*$	
4.78	(15) 0.24	438. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$		2.21	0.10	2.21	0.10	1.52	0.10	4.04	0.20
3.58	0.13	8.0	0.02	4.20	(30) 1.00	2.06	0.50	1.40	0.10	3.87	(17.5) 0.88
3.25	(62.5) 1.00	6.8	0.05	3.97	0.03	1.96	0.10	1.316	0.10	3.57	(20) 1.00
2.56	0.13	6.0	0.02	3.80	(20) 0.67	1.92	0.25	1.233	0.10	2.90	0.20
2.40	0.02	5.5	0.13	3.61	0.07	1.86	0.10	1.185	0.10	2.77	(15) 0.75
2.28	0.13	4.90	(62.5) 1.00	3.43	0.27	1.81	0.05	1.121	0.10	2.50	0.50
2.23	0.10	4.55	0.08	3.15	0.13	1.75	0.10			2.26	0.30
2.05	0.11	4.02	0.08	3.03	(17.5) 0.58	1.70	0.15	449. $\text{PbHAsO}_4$		2.21	0.15
1.99	(12.5) 0.20	3.78	(40) 0.64	2.87	0.03	1.67	0.10	6.7	0.20	2.15	0.50
1.83	0.16	3.23	(12.5) 0.20	2.80	0.27	1.64	0.15	4.88	0.10	2.08	0.50
1.78	0.02	3.09	0.06	2.71	0.03	1.58	0.10	4.43	0.15	1.94	0.45
1.70	0.03	2.92	0.03	2.64	0.03	1.54	0.05	3.39	(20) 1.00	1.63	0.20
1.63	0.20	2.75	0.11	2.56	0.07	1.494	0.20	3.17	(17.5) 0.87	1.58	0.20
1.59	0.20	2.63	0.16	2.52	0.03			2.93	(6) 0.30	1.50	0.05
1.55	0.10	2.50	0.03	2.45	0.23	445. $\text{Pb}^*$		2.56	0.10	1.460	0.10
1.440	0.06	2.42	0.02	2.32	0.03	2.85	(6) 1.00	2.42	0.10	1.425	0.05
1.420	0.02	2.31	0.10	2.23	0.20	2.47	(3) 0.50	2.20	0.20	1.393	0.10
1.361	0.05	2.17	0.02	2.16	0.16	1.74	(3) 0.50	1.95	0.20	1.350	0.05
1.281	0.13	2.11	0.02	2.08	0.13	1.490	0.50	1.78	0.20	1.269	0.05
1.251	0.02	2.07	0.05	2.04	0.03	1.428	0.17	1.68	0.15	1.213	0.05
1.200	0.08	2.01	0.08	1.98	0.07	1.134	0.17	1.55	0.10		
1.140	0.03	1.96	0.08	1.91	0.03	1.105	0.17	1.475	0.10	454. $\text{PbCrO}_4$	
1.110	0.02	1.92	0.02	1.86	0.07			1.390	0.05	4.97	0.23
1.014	0.02	1.87	0.08	1.81	0.03	446. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$		1.338	0.05	4.38	(8) 0.46
1.000	0.03	1.81	0.02	1.76	0.03	11.7	(20) 1.00	1.300	0.05	3.75	0.11
436. $\text{FeSO}_4 \cdot \text{H}_2\text{O}$		1.75	0.05	1.73	0.03	7.7	(8) 0.40	1.275	0.05	3.48	0.40
4.85	(20) 0.50	1.70	0.06	1.69	0.03	4.90	0.30	1.250	0.05	3.28	(17.5) 1.00
3.42	(40) 1.00	1.63	0.05	1.63	0.03	4.36	0.40	1.220	0.10	3.01	(15) 0.86
3.25	0.25	1.56	0.03	1.55	0.03	4.24	0.40	450. $\text{PbBr}_2$		2.71	0.11
3.13	(15) 0.38	1.53	0.03	1.480	0.07	3.50	(20) 1.00	6.0	0.33	2.61	0.11
2.57	0.25	1.50	0.03	1.441	0.03	3.36	0.40	4.18	(5) 0.83	2.53	0.11
2.50	0.25	1.468	0.02	1.384	0.03	2.90	0.25	3.92	0.50	2.32	0.11
2.24	0.15	439. $\text{FeNH}_4(\text{SO}_4)_2 \cdot <12\text{H}_2\text{O}$		1.335	0.03	2.81	0.20	3.72	0.33	2.25	0.34
2.07	0.18			1.254	0.03	2.69	0.10	3.40	(6) 1.00	2.15	0.06
2.00	0.15	9.2	(10) 0.67	1.222	0.03	2.62	0.10	2.94	0.67	2.08	0.17
1.93	0.08	8.2	(7) 0.47	1.197	0.03	2.53	0.10	2.62	0.67	1.97	0.40
1.82	0.08	7.0	(15) 1.00	1.182	0.03	2.43	0.05	2.39	(5) 0.83	1.91	0.06
1.71	0.10	5.9	0.07	1.159	0.03	2.28	0.40	2.29	0.17	1.85	0.34
1.68	0.13	5.5	0.07	1.134	0.03	2.17	0.30	2.21	0.17	1.80	0.06
1.60	0.31	4.72	0.13	1.112	0.03	2.10	0.25	2.12	0.33	1.74	0.06
1.50	0.05	4.51	0.27	442. $\text{FeS}^*$		1.98	0.15	2.05	0.33	1.69	0.11
1.450	0.08	4.14	0.33			1.92	0.05	1.94	0.33	1.65	0.06
1.330	0.03	3.72	0.07	2.97	(25) 0.33	1.88	0.05	1.84	0.33	1.61	0.06
1.290	0.10	3.57	0.13	2.88	(25) 0.04	1.78	0.05	1.76	0.33	1.54	0.06
1.264	0.05	3.40	0.40	2.65	(75) 0.33	1.73	0.10	1.69	0.33	1.422	0.09



(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>						
455. Pb <sub>2</sub> Fe(CN) <sub>6</sub> .3H <sub>2</sub> O				459. PbI <sub>2</sub> *				463. PbO <sub>2</sub> *				468. PbS <sub>2</sub> O <sub>3</sub>				474. Li <sub>2</sub> CO <sub>3</sub>				478. Li <sub>2</sub> CrO <sub>4</sub> .2H <sub>2</sub> O			
7.3		7.0	0.13	3.49	(25)	1.00	4.80	0.33	4.16	(25)	0.63	6.6			0.40								
6.3	(10)	3.95	0.02	2.78	(25)	1.00	4.25	(6)	1.00	3.80	0.05	5.3			0.27								
5.7		3.43	(75)	2.46		0.28	4.02	(6)	1.00	3.02	0.05	4.78			0.83								
4.10	(15)	2.62	(30)	1.84	(25)	1.00	3.61	(4)	0.67	2.91	(20)	0.50	4.50		0.67								
3.67	(15)	2.27	(20)	1.74		0.20	3.41		0.33	2.80	(40)	1.00	4.25		0.83								
3.32		2.16		1.68		0.08	2.91		0.50	2.62		0.25	4.08		0.83								
3.11		2.00		1.56		0.20	2.68		0.50	2.47		0.10	3.70		0.67								
2.99		1.90		1.51		0.24	2.48		0.33	2.42		0.38	3.57		0.67								
2.82		1.71		1.480		0.24	2.37		0.67	2.26		0.18	3.38		0.40								
2.66		1.63		1.390		0.12	2.27		0.33	2.07		0.03	3.18		0.53								
2.42		1.50		1.268		0.16	2.18		0.50	1.86		0.13	3.07	(15)	1.00								
2.14		1.454		1.210		0.08	2.12		0.17	1.81		0.03	3.00	(15)	1.00								
2.05		1.381		1.145		0.08	2.04		0.17	1.61		0.03	2.76	(15)	1.00								
1.91		1.370		1.125		0.08	1.98		0.17	1.59		0.05	2.65		0.27								
1.84		1.314		1.000		0.12	1.92		0.17	1.57		0.05	2.55		0.27								
1.76		1.287		0.948		0.04	1.87		0.17	1.54		0.05	2.49		0.53								
1.67		1.258					1.74		0.17	1.51		0.05	2.37		0.53								
1.63		1.137					1.70		0.17	1.460		0.05	2.18		0.40								
1.56		1.080		464. Pb <sub>3</sub> O <sub>4</sub>			1.65		0.17	1.422		0.03	2.10		0.27								
1.490		1.045					1.59		0.17	1.389		0.03	2.03		0.40								
1.420		1.020		3.35	(7)	1.00	1.382		0.17	1.350		0.03	1.92		0.13								
1.360				2.88	(3)	0.43	1.346			1.311		0.03	1.87		0.07								
1.310				2.76	(3)	0.43							1.81		0.27								
1.243				2.62		0.28							1.75		0.13								
1.208				1.95		0.14							1.70		0.07								
1.181				1.89		0.28							1.66		0.40								
1.158				1.82		0.28							1.63		0.40								
				1.74		0.43							1.59		0.13								
				1.62		0.14							1.53		0.07								
				1.58		0.14							1.50		0.27								
				1.51		0.14							1.452		0.40								
				1.405		0.14							1.400		0.13								
													1.370		0.07								
													1.340		0.13								



(Starred patterns were checked with published crystal structure data)

(Started patterns were checked with published crystal structure data)

$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$
483. $\text{LiI} \cdot 3\text{H}_2\text{O}^*$		487. $\text{Li}(\text{C}_6\text{H}_4\text{OH} \cdot \text{COO})$		491. $\text{LiHC}_4\text{H}_4\text{O}_6$		494. $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$		498. $2\text{MgHAsO}_4 \cdot 13\text{H}_2\text{O}$	
6.4	0.11			5.3	0.10				
4.19	(75) 1.00	11.3	0.07	5.0	0.20	6.9	(50) 1.00	6.0	0.13
3.72	(50) 0.67	8.4	0.07	4.27	1.00	4.78	(10) 0.20	4.87	0.25
3.22	0.23	6.5	0.13	3.70	(6) 0.60	4.47	(10) 0.02	4.25	(40) 1.00
2.78	(75) 1.00	5.4	(12.5) 0.83	3.48	0.10	4.07	0.06	3.90	0.13
2.44	0.17	5.2	0.13	3.35	0.60	3.77	0.02	2.99	(20) 0.50
2.22	0.40	4.86	0.13	3.00	0.20	3.22	(30) 0.60	2.69	0.05
2.15	0.09	4.52	(10) 0.67	2.77	0.10	3.05	0.12	2.44	(25) 0.63
2.08	0.11	4.28	(15) 0.53	2.64	0.20	2.93	0.20	2.36	0.38
2.00	0.03	3.55	1.00	2.56	0.20	2.70	0.02	2.10	0.03
1.86	0.11	3.30	0.20	2.36	(8) 0.80	2.54	0.12	1.88	0.13
1.82	0.11	3.15	0.13	2.29	0.10	2.40	0.10	1.80	0.13
1.75	0.09	2.92	0.07	2.17	0.10	2.28	0.06	1.65	0.03
1.70	0.33	2.82	0.13	2.08	0.10	2.23	0.02	1.60	0.50
1.58	0.11	2.70	0.13	2.02	0.10	2.14	0.14	1.58	0.10
1.54	0.13	2.42	0.07	1.90	0.10	2.08	0.02	1.51	0.10
1.50	0.03	2.31	0.07	1.83	0.10	2.03	0.06	1.486	0.10
1.460	0.05			1.77	0.10	1.95	0.02	1.406	0.08
1.431	0.08			1.74	0.10	1.89	0.10	1.372	0.03
1.409	0.05			1.69	0.10	1.86	0.10	1.332	0.10
1.360	0.01	488. $\text{Li}_2\text{SO}_4^*$				1.80	0.04	1.305	0.03
1.280	0.07	4.01	(62.5) 1.00			1.72	0.04	1.275	0.08
1.256	0.07	3.49	0.11	492. $\text{Mg}^*$		1.67	0.02	1.179	0.05
1.195	0.04	3.16	(25) 0.40			1.63	0.02	1.090	0.03
		2.78	0.06	2.77	(30) 0.30	1.59	0.02	1.060	0.05
484. $\text{LiC}_3\text{H}_5\text{O}_3$		2.68	0.03	2.60	(25) 0.25	1.53	0.02		
11.1	(20) 1.00	2.62	0.05	2.45	(100) 1.00	1.430	0.02		
5.5	0.05	2.47	(8) 0.13	1.90	0.20	1.410	0.02		
5.3	0.10	2.40	0.06	1.60	0.20	1.360	0.02	499. $\text{Mg}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$	
4.90	0.05	2.31	0.06	1.471	0.20	1.269	0.02		
4.50	0.05	2.20	0.03	1.378	0.18	1.170	0.02		
4.30	(6) 0.30	2.09	0.05	1.341	0.13			14.8	(15) 1.00
4.04	0.20	2.01	0.02	1.303	0.03			10.3	0.13
3.73	(6) 0.15	1.95	0.13	1.225	0.03	495. $\text{Mg}_2\text{Al}_3$		7.8	0.13
3.30	0.30	1.88	0.05	1.180	0.03			6.8	0.27
3.13	0.05	1.81	0.03	1.084	0.04	2.47	(75) 1.00	6.0	(12.5) 0.84
2.90	0.05	1.77	0.02	1.030	0.07	2.38	(40) 0.53	4.82	0.13
2.65	0.10	1.67	0.02	1.010	0.03	2.32	0.17	4.45	(12.5) 0.84
2.48	0.15	1.60	0.03	0.974	0.04	2.21	0.20	4.12	0.13
2.24	0.10	1.56	0.02	0.925	0.01	2.12	0.13	3.73	0.10
2.12	0.10	1.53	0.03	0.898	0.03	2.05	0.05	3.57	0.10
		1.487	0.06	0.870	0.01	1.99	0.04	3.38	0.13
		1.424	0.02	0.763	0.01	1.94	0.03	3.25	0.27
		1.400	0.03	0.740	0.01	1.94	0.03	3.13	0.13
		1.340	0.03			1.57	0.07	2.93	0.10
		1.279	0.03			1.490	0.17	2.74	0.20
485. $\text{LiNO}_3^*$		1.215	0.02	493. $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$		1.423	(30) 0.40	2.58	0.07
3.58	(50) 0.67	1.185	0.03			1.325	0.05	2.38	0.07
2.78	(40) 0.53			9.8	0.13	1.240	0.07	2.22	0.07
2.53	0.20	489. $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}^*$		8.9	1.00	1.215	0.08	2.16	0.07
2.13	(75) 1.00	7.8	0.07	6.3	(30) 0.03	1.138	0.03	2.06	0.07
1.95	0.01	5.1	(20) 0.67	5.5	0.13	1.105	0.03	2.01	0.07
1.72	0.11	4.12	(30) 1.00	5.3	0.03	1.030	0.03	1.94	0.07
1.53	0.27	3.84	0.58	4.37	0.07	0.972	0.03	1.87	0.07
1.420	0.01	3.68	0.07	4.15	0.07	0.928	0.01		
1.371	0.20	3.54	(20) 0.67	3.95	0.05				
1.355	0.13	3.02	0.50	3.51	(10) 0.33				
1.255	0.04	2.93	0.33	3.30	0.20	496. $\text{Mg}_3\text{Al}_2^*$		500. Magnesium Borate	
1.194	0.04	2.72	0.33	3.14	0.03				
1.140	0.01	2.65	0.03	3.01	0.03	2.80	0.01B	7.7	0.12
1.117	0.03	2.48	0.03	2.89	0.20	2.64	(150) 1.00	6.1	0.16
1.082	0.04	2.41	0.27	2.76	(6) 0.05	2.48	(50) 0.33	5.3	0.08
1.025	0.01	2.33	0.03	2.58	0.10	2.24	0.12	4.29	0.24
1.008	0.03	2.28	0.03	2.43	0.10	2.15	0.20	3.57	0.12
0.982	0.03	2.18	0.07	2.33	0.03	2.06	0.01	3.18	0.12
0.932	0.01	2.04	0.07	2.19	0.13	1.92	0.01	3.07	(10) 0.80
0.927	0.01	1.91	0.07	2.10	0.03	1.81	0.01	2.82	(12.5) 1.00
0.895	0.01	1.81	0.07	2.04	0.05	1.75	0.01	2.18	0.24
0.890	0.01	1.72	0.07	1.98	0.03	1.71	0.01	2.07	0.32
		1.70	0.07	1.91	0.03	1.60	0.02	1.99	(5) 0.40
		1.63	0.03	1.88	0.03	1.52	0.05	1.91	0.08
486. $\text{Li}_2\text{C}_2\text{O}_4$		1.59	0.07	1.82	0.03	1.490	0.10	1.86	0.12
4.49	(40) 0.53	1.55	0.07	1.76	0.05	1.434	(50) 0.33	1.77	0.08
3.29	0.12	1.490	0.07	1.68	0.03	1.412	0.04	1.71	0.08
3.08	0.23	1.378	0.07	1.65	0.03	1.386	0.05	1.63	0.12
2.83	0.09			1.61	0.03	1.342	0.06	1.50	0.08
2.75	(25) 0.33			1.55	0.03	1.245	0.10	1.445	0.08
2.64	(75) 1.00	490. $\text{Li}_2\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$		1.50	0.03	1.195	0.01	1.412	0.08
2.57	0.17	5.6	0.13			1.165	0.03	1.375	0.08
2.25	0.12	4.57	(8) 1.00			1.140	0.03	1.262	0.16
2.15	0.20	4.06	(5) 0.63			1.115	0.04	1.151	0.08
2.05	0.13	3.80	(8) 1.00						
1.97	0.01	3.55	0.25			497. $\text{MgAl}_2\text{O}_4^*$		501. $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$	
1.82	0.03	3.42	0.25						
1.74	0.09	3.30	0.13			4.63	0.13	4.25	(12.5) 0.83
1.69	0.27	2.97	0.13			2.83	0.30	4.03	0.07
1.61	0.09	2.84	0.13			2.41	(100) 1.00	3.68	0.40
1.53	0.01	2.75	0.13			2.31	0.02	3.11	(8) 0.53
1.498	0.03	2.59	0.25			2.00	(62.5) 0.63	3.00	0.40
1.466	0.09	2.43	0.13			1.63	0.08	2.80	0.47
1.420	0.04	2.38	0.13			1.54	0.40	2.71	(15) 1.00
1.380	0.04	2.24	0.13			1.417	(75) 0.75	2.40	0.07
1.290	0.03	2.15	0.13			1.358	0.01	2.37	0.13
1.244	0.07	2.08	0.13			1.268	0.02	2.33	0.27
1.205	0.01	2.00	0.13			1.223	0.06	2.21	0.20
		1.93	0.13			1.158	0.03	2.11	0.20
		1.83	0.13			1.067	0.02	1.98	0.13
		1.77	0.13			1.040	0.08	1.90	0.40
		1.66	0.13			0.998	0.03	1.78	0.20
		1.59	0.13			0.941	0.01	1.72	0.13
		1.480	0.13			0.923	0.02	1.67	0.13
		1.425	0.13			0.893	0.01	1.63	0.13
						0.838	0.02	1.57	0.07
						0.817	0.04	1.55	0.13
						0.773	0.02		



(Starred patterns were checked with published crystal structure data)

(Started patterns were checked with published crystal structure data)

<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>	<i>d</i>	<i>I/I<sub>1</sub></i>
507. $\text{Mg}(\text{ClO}_4)_2$		512. $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$		515. $\text{MgF}_2 \cdot *$		519. $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$		523. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$		528. $(\text{C}_6\text{H}_5\text{OHSO}_3)_2\text{Mg}$			
6.9	0.10			3.29	(100) 0.80	7.9	0.12	11.0	0.05				
4.90	(25) 0.63	6.7	0.18	3.14	0.05	6.0	0.08	8.9	0.05	6.1	0.16		
3.39	(40) 1.00	4.75	0.03	2.56	0.20	5.0	0.20	6.2	0.05	5.6	0.08		
3.20	0.23	4.30	0.03	2.24	(125) 1.00	4.31	(12.5) 0.25	5.8	0.20	4.70	(8) 0.64		
2.69	0.05	3.85	(30) 0.75	2.07	0.32	4.09	(50) 1.00	4.42	(40) 1.00	4.29	(5) 0.40		
2.60	(10) 0.25	3.33	(40) 1.00	1.93	0.12	3.75	0.08	4.18	0.25	3.95	(12.5) 1.00		
2.17	0.08	2.97	0.50	1.72	(125) 1.00	3.50	0.12	3.57	0.18	3.50	0.16		
2.04	0.13	2.73	(30) 0.75	1.64	0.32	3.23	0.12	3.29	(17.5) 0.44	3.15	0.24		
1.90	0.05	2.48	0.03	1.53	0.20	3.03	(17.5) 0.35	3.18	0.13	2.84	0.24		
1.80	0.08	2.35	0.50	1.460	0.05	2.80	0.20	3.10	0.05	2.57	0.24		
1.71	0.03	2.23	0.18	1.437	0.01	2.65	0.02	2.93	(20) 0.50	2.30	0.08		
1.68	0.03	2.10	0.13	1.408	0.01	2.60	0.08	2.85	0.10	2.16	0.08		
1.61	0.13	2.00	0.63	1.378	0.60	2.50	0.12	2.78	0.08				
		1.94	0.15	1.340	0.01	2.42	0.16	2.69	0.20	529. $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$			
508. $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$		1.90	0.15	1.319	0.08	2.35	0.10	2.61	0.10	5.9	(10) 0.40		
6.9	0.02	1.77	0.05	1.227	0.06	2.29	0.04	2.37	0.15	5.3	0.20		
5.5	0.12	1.73	0.05	1.155	0.02	2.23	0.04	2.31	0.08	4.70	0.40		
4.80	(50) 1.00	1.67	0.13	1.116	0.16	2.15	0.16	2.20	0.05	4.15	0.24		
3.99	(30) 0.60	1.58	0.15	1.090	0.05	2.05	0.08	2.12	0.15	3.64	0.08		
3.35	(30) 0.60	1.53	0.10	1.052	0.06	2.03	0.08	2.07	0.08	3.45	(25) 1.00		
3.22	(50) 1.00	1.490	0.23			1.98	0.10	2.03	0.04	3.05	(20) 0.80		
3.06	0.02	1.370	0.15	516. $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$		1.89	0.02	1.97	0.03	2.80	0.32		
2.95	0.04	1.349	0.05			1.85	0.04	1.92	0.04	2.71	0.24		
2.85	0.06	1.285	0.10	6.4	0.08	1.75	0.14	1.86	0.03	2.57	0.32		
2.75	0.08	1.224	0.05	5.3	0.03	1.67	0.12	1.82	0.05	2.39	0.24		
2.59	0.20	1.180	0.03	4.79	(62.5) 1.00	1.63	0.12	1.77	0.03	2.20	0.12		
2.43	0.04	1.120	0.05	4.54	(20) 0.32	1.60	0.12	1.73	0.03	2.05	0.12		
2.34	0.10			4.22	(17.5) 0.06	1.57	0.02	1.69	0.04	1.97	0.04		
2.25	0.02	513. $\text{MgCrO}_4 \cdot 7\text{H}_2\text{O}$		2.98		1.51	0.02	1.65	0.03	1.92	0.08		
2.18	0.02			2.64		1.465	0.04			1.87	0.16		
2.03	0.12	10.8	0.20	2.33		1.432	0.04	524. $\text{Mg}_3\text{N}_2 \cdot *$		1.79	0.04		
1.99	0.10	6.0	(12.5) 0.42	2.24	0.05			4.08	0.13	1.75	0.04		
1.90	0.14	5.0	(30) 1.00	2.10	0.02	520. $\text{Mg}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$		2.87	0.20	1.66	0.08		
1.84	0.16	4.45	0.27	1.92	0.13			2.66	(40) 0.27	1.59	0.08		
1.76	0.02	4.08	0.20	1.87	0.02	9.5	(12.5) 1.00	2.49	0.20	1.490	0.04		
1.72	0.04	3.77	(15) 0.50	1.81	0.03	5.1	(10) 0.80	2.12	(62.5) 0.42	1.410	0.08		
1.67	0.02	3.60	0.13	1.77	0.06	4.52	0.24	1.95	0.03	1.380	0.04		
1.62	0.10	3.36	0.30	1.67	0.02	3.68	(4) 0.32	1.81	0.01	1.325	0.04		
		3.23	0.20	1.64	0.02	3.48	0.24	1.76	(150) 1.00				
509. $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$		3.12	0.27	1.60	0.02	3.00	0.16	1.61	0.03	530. $\text{Mg}(\text{H}_2\text{PO}_4)_2$			
6.8	0.02	2.99	0.33	1.50	0.02	2.70	0.08	1.53	0.03	4.95	0.16		
4.91	0.05	2.86	0.30	1.425	0.02	2.19	0.16	1.50	0.02	4.47	0.60		
4.18	(100) 0.80	2.76	0.42	1.401	0.02	1.96	0.08	1.471	0.03	4.08	0.50		
3.91	(75) 0.60	2.61	0.27	1.384	0.02	1.84	0.08	1.438	0.02	3.75	0.12		
3.41	0.03	2.48	0.07	1.330	0.02			1.355	0.20	3.60	0.20		
2.85	(125) 1.00	2.40	0.07	1.255	0.02	521. $\text{Mg}_2\text{Pb} \cdot *$		1.265	0.12	3.37	(20) 0.80		
2.64	0.24	2.31	0.20	1.228	0.02			1.243	0.01	3.14	(25) 1.00		
2.55	0.24	2.23	0.03			517. $\text{Mg}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$		1.132	0.01	2.98	0.60		
2.45	0.06	2.12	0.17			3.91	(15) 1.00	1.111	0.01	2.64	0.28		
2.30	0.24	2.06	0.13			3.39	0.20	1.074	0.02	2.55	0.24		
2.07	0.10	2.00	0.10	4.93	(10) 1.00	2.40	(10) 0.66	1.048	0.01	2.33	(17.5) 0.70		
1.95	0.16	1.95	0.07	4.62	(8) 0.80	2.04	(10) 0.66	1.027	0.02	2.24	0.16		
1.83	0.20	1.92	0.20	4.35	0.30	1.96	0.07	1.015	0.02	2.16	0.04		
1.76	0.20	1.88	0.03	4.37	0.30	1.69	0.07			2.03	0.04		
1.70	0.08	1.88	0.13	3.68	0.60	1.56	0.26	525. $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$		1.94	0.24		
1.60	0.02	1.78	0.10	3.37	(6) 0.20	1.52	0.13	4.90	(30) 1.00	1.84	0.04		
1.56	0.08	1.71	0.10	3.06	0.20	1.387	0.20	3.20	(15) 0.50	1.72	0.12		
1.53	0.02			2.94	0.10	1.307	0.20	2.61	0.07	1.64	0.08		
1.480	0.10	514. $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 14\text{H}_2\text{O}$		2.79	0.10	1.200	0.07	2.54	0.07	1.56	0.12		
1.420	0.06			2.62	0.60	1.148	0.13	2.37	0.20	1.425	0.12		
1.385	0.02	8.4	0.13	2.46	0.10	1.131	0.07	2.07	0.13	1.355	0.04		
1.300	0.08	6.8	0.13	2.32	0.40	1.073	0.07	2.02	0.07	1.315	0.08		
1.280	0.03	6.3	0.03	2.21	0.20	1.035	0.07	1.85	(8) 0.27	1.270	0.04		
1.242	0.04	6.0	0.10	2.07	0.40	0.949	0.07	1.76	0.03	1.195	0.08		
1.183	0.03	5.7	(30) 1.00	1.96	0.10			1.59	0.03	1.160	0.08		
1.162	0.03	5.2	0.13	1.83	0.10	522. $\text{Mg}_3\text{Hg}$		1.52	0.13	1.130	0.04		
		4.90	0.33	1.77	0.10	4.25	0.30	1.345	0.03	531. $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$			
510. $\text{MgCl}_2 \cdot *$		4.50	0.17	1.70	0.10	3.75	(20) 1.00	1.230	0.03	6.1	0.20		
5.9	(25) 0.63	4.10	0.23	1.63	0.10	2.98	0.15			5.2	(4) 0.80		
2.94	0.31	3.75	0.23	1.52	0.10	2.36	(15) 0.75	2.42	0.06	4.10	(5) 1.00		
2.55	(25) 0.63	3.58	0.03	1.420	0.10	2.09	(7) 0.35	2.10	(100) 1.00	3.23	(4) 0.80		
1.96	0.05	3.40	(20) 0.67	1.350	0.10	2.02	0.25	1.485	(75) 0.75	3.09	0.60		
1.80	(40) 1.00	3.10	0.13			1.68	0.15	1.266	0.06	2.87	0.40		
1.72	0.18	2.87	(25) 0.83	518. $\text{Mg}(\text{OH})_2 \cdot *$		1.55	0.10	1.213	(15) 0.15	2.73	0.40		
1.53	0.18	2.74	0.03	4.75	(40) 0.53	1.438	0.10	1.050	0.04	2.65	0.80		
1.470	0.18	2.68	0.03	2.35	(75) 1.00	1.325	0.10	0.963	0.01	2.51	0.40		
1.272	0.05	2.62	0.03	1.79	(30) 0.40	1.265	0.05	0.940	0.10 $\alpha_1$	2.34	0.40		
1.140	0.20	2.54	0.03	1.57	0.33	1.230	0.05	0.937	0.05 $\alpha_2$	1.91	0.20		
1.040	0.08	2.48	0.23	1.490	0.17	1.160	0.05	0.860	0.04 $\alpha_1$	1.79	0.20		
0.983	0.05	2.40	0.17	1.370	0.13			0.854	0.02 $\alpha_2$	1.74	0.20		
		2.35	0.09	1.306	0.07								
		2.24	0.03	1.183	0.07								
		2.13	0.13	1.031	0.03								
		2.05	0.07	1.005	0.04								
		2.00	0.07	0.945	0.04								
		1.94	0.20	0.862	0.01								
		1.88	0.13										
		1.82	0.07										
		1.77	0.07										
		1.73	0.07										
		1.69	0.13										
		1.59	0.07										
		1.56	0.03										
		1.52	0.03										
		1.480	0.03										
		1.446	0.03										
		1.415	0.03										
		1.334	0.05										



(Starred patterns were checked with published crystal structure data)

[illegible]



(Starred patterns were checked with published crystal structure data)

[illegible]



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)																	
d	I/I <sub>1</sub>		d	I/I <sub>1</sub>		d	I/I <sub>1</sub>		d	I/I <sub>1</sub>		d	I/I <sub>1</sub>				
584. Hg <sub>2</sub> Cl <sub>2</sub> *			589. Hg(CN) <sub>2</sub> *			593. HgNO <sub>3</sub> .H <sub>2</sub> O			597. Hg <sub>3</sub> PO <sub>4</sub>			601. Hg <sub>2</sub> SO <sub>4</sub>			606. H <sub>2</sub> MoO <sub>4</sub>		
4.16	(50)	1.00	4.85	(12.5)	0.83	6.6		0.17	7.2		0.11	4.42	(12.5)	0.63	10.9		0.50
3.17	(50)	1.00	3.72	(15)	1.00	5.6	(17.5)	1.00	6.3		0.22	4.19	(12.5)	0.63	8.9		0.63
2.83		0.08	3.42		0.13	4.75		0.11	5.5		0.22	3.61		0.10	7.7		0.50
2.72		0.30	3.03		0.10	4.20		0.11	4.83		0.44	3.47		0.05	6.6	(40)	1.00
2.24		0.30	2.86		0.07	3.75	(5)	0.29	4.40		0.56	3.11		0.10	5.9		0.25
2.06		0.60	2.58		0.10	3.47	(7)	0.40	3.85		0.44	3.03	(20)	1.00	5.3		0.15
1.97	(40)	0.80	2.51	(10)	0.67	3.20		0.17	3.60		0.33	2.85		0.05	5.0		0.15
1.73		0.35	2.42		0.13	3.10		0.17	3.48		0.44	2.73		0.10	4.71		0.18
1.58		0.08	2.28		0.10	2.80		0.23	3.09	(6)	0.67	2.55		0.25	4.34		0.05
1.478		0.40	2.22		0.07	2.67		0.06	2.94	(8)	0.89	2.37		0.10	4.10		0.38
1.417		0.16	2.17		0.13	2.50		0.17	2.72		0.22	2.20		0.30	3.47	(40)	1.00
1.366		0.16	2.02		0.33	2.38		0.17	2.60	(9)	1.00	2.08		0.30	3.30		0.63
1.260		0.20	1.90		0.10	2.32		0.17	2.45		0.22	2.01		0.05	3.06	(30)	0.75
1.237		0.06	1.86		0.07	2.24		0.23	2.28		0.44	1.96		0.10	2.90		0.38
1.171		0.16	1.76		0.10	2.17		0.06	2.18		0.17	1.89		0.25	2.77		0.20
1.127		0.02	1.68		0.07	2.09		0.11	2.12		0.22	1.80		0.10	2.63		0.13
1.083		0.06	1.61		0.10	1.96		0.23	2.01		0.17	1.73		0.15	2.55		0.25
1.060		0.02	1.56		0.10	1.91		0.06	1.94		0.22	1.66		0.05	2.44		0.25
1.038		0.14	1.487		0.07	1.87		0.06	1.89		0.11	1.62		0.05	2.37		0.18
1.003		0.02	1.455		0.07	1.82		0.11	1.86		0.17	1.52		0.10	2.32		0.20
0.987		0.02	1.425		0.07	1.79		0.11	1.81		0.17				2.24		0.25
0.942		0.02	1.399		0.07	1.74		0.06	1.77		0.17				2.19		0.10
						1.68		0.06	1.66		0.22				2.10		0.10
						1.61		0.11	1.62		0.11	602. HgS* (cubic)			2.02		0.13
									1.57		0.22				1.95		0.38
									1.52		0.22	3.37	(50)	1.00	1.85		0.05
									1.50		0.22	2.92		0.16	1.80		0.18
									1.440		0.22	2.06	(15)	0.30	1.69		0.18
									1.384		0.11	1.76	(15)	0.30	1.64		0.05
									1.346		0.11	1.69		0.04	1.59		0.15
												1.460		0.02	1.53		0.13
												1.340		0.08			
												1.305		0.06			
												1.191		0.04			
												1.124		0.04			
															607. Mo <sub>2</sub> C*		
									7.1	(30)	1.00				2.60		0.29
									6.5		0.03				2.36		0.24
									6.1		0.03				2.28	(212.5)	1.00
									5.6		0.03				1.75		0.24
									4.38		0.13	3.36	(62.5)	0.83	1.50	(75)	0.35
									4.05		0.13	3.16		0.27	1.350	(75)	0.35
									3.80	(5)	0.17	2.85	(75)	1.00	1.300		0.03
									3.62	(15)	0.50	2.35		0.08	1.267		0.35
									3.47		0.13	2.06		0.27	1.259		0.35
									3.22		0.07	1.97	(25)	0.33	1.182		0.04
									3.02		0.10	1.89		0.01	1.142		0.06
									2.81		0.07	1.76		0.11	1.079		0.04
									2.62		0.07	1.72		0.20	1.005		0.07
									2.48		0.07	1.67		0.27	0.983		0.03
									2.37		0.07	1.57		0.08B	0.965		0.19
									2.19		0.07	1.429		0.09	0.930		0.09
									2.12		0.13	1.395		0.03	0.907		0.05
									2.03		0.10	1.340		0.11	0.892		0.05
									1.98		0.05	1.300		0.13	0.872		0.04
									1.93		0.07	1.252		0.11	0.837		0.08
									1.88		0.03	1.179		0.04B	0.818		0.05
									1.77		0.03	1.121		0.05			
									1.67		0.03	1.100		0.05			
									1.62		0.03	1.080		0.01			
									1.51		0.03	1.027		0.03			
									1.404		0.03				608. Molybdenum Oxalate		
									1.372		0.03				8.4		0.27
									1.320		0.03				5.2	(75)	1.00
									1.272		0.03				4.41	(50)	0.67
									1.242		0.03				4.17		0.17
												6.5	(15)	0.75	3.77	(40)	0.53
												5.4		0.75	3.30		0.53
												4.37		0.75	3.09		0.08
												3.97		0.10	2.99		0.12
												3.80	(20)	1.00	2.90		0.08
												3.32		0.75	2.77		0.17
												2.88		0.05	2.59		0.11
												2.67		0.40	2.46		0.13
												2.56		0.50	2.17		0.20
												2.42		0.20	2.14		0.20
												2.14		0.20	2.07		0.13
												2.02		0.20	1.91		0.23
												1.98		0.20	1.87		0.08
												1.92		0.20	1.78		0.07
												1.89		0.20	1.74		0.03
												1.83					



(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>		
609. MoO <sub>3</sub> *		613. NdCl <sub>3</sub> ·6H <sub>2</sub> O		616. Ni(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>		620. NiCl <sub>2</sub> ·4H <sub>2</sub> O		623. Nickel Fluoride		626. Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O			
6.9	0.24	(20)	1.00	7.4	0.05	5.4	0.31	4.85	(50)	1.00	7.2	0.07	
3.80	(75)	6.0	(12.5)	6.9	(40)	4.80	(25)	4.10	(25)	0.50	5.5	(30)	1.00
3.46	(50)	5.4	0.50	5.9	0.03	4.29	(40)	3.78	0.04	5.1	0.23		
3.25	(125)	5.1	0.50	4.75	12.5	3.95	0.20	3.11	(25)	0.30	4.40	0.07	
3.00	0.06	4.85	0.20	4.48	0.03	3.63	0.03	2.98	0.50	4.14	0.20		
2.66	0.32	4.56	0.30	4.25	0.08	3.40	0.03	2.75	0.20	3.78	(30)	1.00	
2.52	0.08	4.41	0.30	4.00	(10)	3.17	0.05	2.53	0.12	3.40		0.33	
2.30	0.32	3.98	0.45	3.82	0.15	2.94	0.31	2.44	0.14	3.12		0.10	
2.26	0.06	3.60	0.35	3.57	0.13	2.83	(20)	2.31	0.10	2.90		0.20	
2.13	0.06	3.43	(20)	3.14	0.25	2.70	0.38	2.22	0.12	2.74	(15)	0.50	
1.97	0.24	3.13	0.20	3.03	0.05	2.60	0.15	2.15	0.50	2.62		0.03	
1.97	0.24	2.88	0.25	2.95	0.03	2.52	0.38	2.00	0.30	2.55		0.20	
1.85	0.16	2.67	0.05	2.87	0.15	2.41	0.18	1.93	0.16	2.37		0.17	
1.73	0.04	2.61	0.10	2.71	0.05	2.34	0.03	1.88	0.08	2.28		0.10	
1.70	0.12	2.54	0.10	2.50	0.15	2.27	0.03	1.78	0.16	2.21		0.05	
1.67	0.12	2.47	0.05	2.41	0.05	2.21	0.03	1.74	0.25	2.16		0.10	
1.63	0.12	2.42	0.35	2.30	0.13	2.14	0.13	1.69	0.04	2.06		0.03	
1.60	0.14	2.36	0.05	2.18	0.08	2.09	0.13	1.65	0.08	1.99		0.07	
1.57	0.03	2.30	0.25	2.11	0.10	2.00	0.31	1.59	0.08	1.89		0.07	
1.50	0.08	2.14	0.35	2.06	0.03	1.95	0.31	1.53	0.08	1.84		0.10	
1.475	0.20	2.07	0.20	2.01	0.08	1.91	0.18	1.487	0.04	1.70		0.05	
1.440	0.06	2.00	0.05	1.96	0.03	1.83	0.44	1.460	0.10	1.65		0.05	
1.395		1.96	0.25	1.91	0.05	1.76	0.20	1.438	0.04	1.60		0.03	
		1.92	0.25	1.86	0.08	1.70	0.15	1.400	0.06				
		1.87	0.05	1.80	0.04	1.65	0.15	1.368	0.08				
		1.84	0.05	1.74	0.03	1.55	0.13	1.310	0.02				
3.42	(125)	1.00	0.05	1.70	0.03	1.52	0.08	1.260	0.06				
2.42	(100)	0.80	0.10	1.66	0.04	1.470	0.03	1.215	0.06				
2.22		0.40	0.05	1.61	0.03	1.420	0.05	1.188	0.04				
2.17		0.03	0.10	1.58	0.03	1.403	0.08	1.160	0.04				
1.84		0.06	0.10	1.52	0.03	1.355	0.08	1.121	0.02				
1.71	(100)	0.80	0.05	1.52	0.03	1.318	0.08						
1.57	0.06	1.480	0.05	1.480	0.03	1.318	0.08						
1.53	0.16	1.439	0.05	1.440	0.04	1.277	0.05						
1.470	0.03	1.416	0.05	1.410	0.03								
1.405	0.20	1.390	0.05	1.166	0.03								
1.350	0.02	1.358	0.05			621. NiCl <sub>2</sub> ·6H <sub>2</sub> O		Ni(CHO <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O					
1.305	0.02	1.330	0.05			5.5	(50)	1.00	(30)	0.75			
1.285	0.24	1.300	0.10	617. NiAl <sub>2</sub> O <sub>4</sub> *		4.85	(50)	1.00	(40)	1.00			
1.211	0.16	1.272	0.05			3.53	(25)	0.50		0.20			
1.180	0.02	1.251	0.05	2.43	(6)	3.08		0.04		0.03	2.40	(75)	0.60
1.141	0.06			2.01	(6)	2.95		0.50		0.03	2.08	(125)	1.00
1.114	0.06			1.55		2.70		0.34		0.25	1.474	(75)	0.60
1.087	0.04	614. Neodymium Ammonium Nitrate		1.421	(8)	2.54		3.12		0.03	1.258		0.24
1.032	0.02					2.40		3.02		0.03	1.203		0.12
1.015	0.01	9.7	0.03	618. NiCl <sub>2</sub> *		2.18		2.78		0.15	1.042		0.02
0.997	0.06	8.8	(30)	1.00		2.05		2.70		0.03	0.957		0.04
0.976	0.02	7.8		0.03	5.7	(50)	0.67	2.58	(15)	0.38	0.933		0.05
0.955	0.02	6.9	(30)	1.00	2.96	(30)	0.40	2.42		0.15	0.852		0.03
0.920	0.06	6.2		0.07	2.46	(75)	1.00	2.27		0.15	0.802		0.02
0.880	0.02	5.7		0.27	2.27		0.07	2.18		0.10			
0.857	0.05	5.4	(10)	0.33	1.91		0.13	2.12		0.08			
0.842	0.05	5.2		0.27	1.74		0.40	2.03		0.15			
		4.44		0.07	1.66		0.17	1.91		0.10	4.85		0.12
		4.23		0.30	1.495		0.03	1.83		0.08	2.97		0.30
		3.93		0.23	1.440		0.01	1.76		0.08	2.53	(50)	1.00
		3.56		0.17	1.419		0.09	1.68		0.15	2.41		0.25
		3.33		0.17	1.390		0.03	1.63		0.08	2.09	(25)	0.50
		3.14		0.33	1.284		0.03	1.59		0.03	1.71		0.08
		2.94		0.10	1.232		0.04	1.56		0.03	1.61		0.40
		2.81		0.33	1.131		0.01	1.54		0.03	1.480	(30)	0.60
		2.68		0.03	1.109		0.01	1.50		0.05	1.280		0.08
		2.63		0.07	1.100		0.08	1.460		0.03	1.260		0.12
		2.53		0.10	1.030		0.01	1.399		0.03	1.207		0.08
		2.44		0.20	1.003		0.04	1.380		0.05	1.119		0.04
		2.38		0.13				1.355		0.03	1.090		0.10
		2.33		0.03	619. NiCl <sub>2</sub> ·2H <sub>2</sub> O*			1.340		0.03	1.048		0.04
		2.28		0.13	5.4	(40)	0.80	1.312		0.03			
		2.21		0.13	4.42	(30)	0.60	1.279		0.05			
		2.15		0.23	3.45		0.06	1.230		0.03			
		2.02		0.20	2.91		0.50	1.210		0.03	6.4		0.04
		1.90		0.20	2.74		0.40	1.166		0.03	4.6	(12.5)	0.25
		1.84		0.03	2.44	(50)	1.00	1.141		0.03	4.26	(50)	1.00
		1.80		0.07	2.21		0.40	1.114		0.03	3.96		0.02
		1.76		0.10	2.16		0.06	1.087		0.03	3.77		0.02
		1.69		0.10	2.11		0.40	1.069		0.03	3.38		0.12
		1.63		0.03	1.87		0.25B	1.016		0.03	3.22		0.02
		1.59		0.07	1.72		0.50			0.03	3.18		0.02
		1.56		0.03	1.66		0.35			0.07	2.96		0.18
		1.53		0.03	1.63		0.35			0.27	2.72	(10)	0.20
		1.51		0.03	1.61		0.35			0.03	2.57		0.20
		1.470		0.07	1.52		0.14			0.03	2.34		0.16
		1.440		0.03	1.465		0.12			0.03	2.13		0.20
		1.410		0.07	1.389		0.06			0.03	2.07		0.02
		1.380		0.03	1.359		0.16			0.13	2.02		0.04
		1.345		0.03	1.317		0.06			0.03	1.98		0.02
		1.295		0.07	1.271		0.10			0.03	1.89		0.10
					1.245		0.02			0.03	1.85		0.04
					1.219		0.12			0.17	1.83		0.02
										0.03	1.80		0.02
										0.03	1.75		0.10
										0.03	1.70		0.08
										0.03	1.65		0.08
										0.03	1.59		0.04
										0.03	1.54		0.02
										0.03	1.51		0.04
										0.03	1.470		0.02
										0.03	1.393		0.02
										0.03	1.354		0.02
										0.03	1.301		0.02
										0.03	1.280		0.02
										0.03	1.262		0.02
										0.03	1.250		0.02
										0.03	1.216		0.02
										0.03	1.188		0.02
										0.03	1.164		0.02
										0.03	1.147		0.02
										0.03	1.130		0.02
										0.03	1.112		0.02
										0.03	1.035		0.02
										0.03			
										0.03			
										0.03			
										0.03			
										0.03			
										0.03			
										0.03			
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										0.03			
										0.03			
										0.03			
										0.03			
										0.03			







TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data)													
d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
654. KN <sub>3</sub> *				659. K <sub>2</sub> CO <sub>3</sub>		664. K <sub>2</sub> CrO <sub>4</sub> *		668. KCN*		672. KF*		676. KIO <sub>3</sub> *	
4.33		0.07	7.0		0.02	5.2	0.06	3.77	0.10	3.08	(40)	0.27	4.47
3.05	(25)	0.33	5.5		0.02	4.28	(20)	0.32	3.26	(100)	1.00		(50)
2.75	(75)	1.00	3.39		0.06	3.81		0.13	2.30	(62.5)	0.63		(100)
2.55	(10)	0.13	2.97	(10)	0.16	3.07	(20)	0.32	1.96	(12.5)	0.13		(30)
2.32		0.12	2.80	(62.5)	1.00	2.96	(62.5)	1.00	1.88		0.10		
2.16		0.13	2.61	(20)	0.32	2.57		0.13	1.63		0.06		
1.93		0.11	2.37		0.16	2.47		0.11	1.493		0.06		
1.85		0.05	2.31		0.08	2.28		0.28	1.458		0.09		
1.78		0.07	2.18		0.06	2.14		0.24	1.327		0.05		
1.70		0.12	2.09		0.14	1.92		0.06	1.252		0.03		
1.65		0.01	1.99		0.10	1.82		0.03	1.100		0.01		
1.53		0.08	1.85		0.08	1.72		0.05					
1.403		0.05	1.77		0.03	1.66		0.02					
1.370		0.08	1.70		0.03	1.61		0.03					
1.335		0.07	1.67		0.02	1.475		0.03B					
1.308		0.04	1.61		0.03	1.390		0.05					
1.270		0.01	1.55		0.02	1.325		0.02B					
1.139		0.04	1.50		0.02	1.280		0.02					
1.082		0.04	1.410		0.05	1.250		0.02					
1.009		0.01	1.345		0.02	1.203		0.02					
			1.307		0.02	1.170		0.02					
655. K(C <sub>6</sub> H <sub>5</sub> COO) <sub>3</sub> ·3H <sub>2</sub> O				660. KHCO <sub>3</sub>		665. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		669. K <sub>3</sub> Fe(CN) <sub>6</sub> *		673. KF·2H <sub>2</sub> O		677. KIO <sub>3</sub> ·HIO <sub>3</sub>	
5.7		0.10	7.33		0.20	4.83	0.10	6.7	0.03	4.42	(12.5)	0.63	5.6
5.4		0.10	3.68	(8)	0.32	3.68	0.50	5.9	0.03	4.08		0.10	5.0
5.1		0.10	3.10		0.04	3.45	0.50	5.2	0.03	3.71		0.40	4.30
4.64		0.05	2.95		0.28	3.29	(20)	3.99	0.05	3.37		0.35	4.00
4.23		0.05	2.84	(25)	1.00	3.02	(15)	3.71	0.02	3.20		1.00	3.32
3.89		0.05	2.62	(8)	0.32	2.85	(12.5)	3.36	0.02	3.01	(20)	0.83	3.27
3.75	(10)	0.50	2.37		0.08	2.75		3.21	0.02	2.58	(15)	0.75	2.85
3.55		0.05	2.28		0.24	2.69		3.09	0.02	2.48		0.05	2.75
3.29		0.20	2.21		0.16	2.62		(30)	0.48	2.22		0.05	2.49
3.21	(20)	1.00	2.02		0.12	2.53		(30)	0.48	2.17		0.20	2.02
3.12		0.05	1.96		0.04	2.45			0.02	2.12		0.50	1.97
3.00		0.10	1.84		0.12	2.38			0.06	1.94		0.40	1.88
2.90		0.05	1.80		0.06	2.29			0.48	1.86		0.05	1.73
2.84		0.05	1.75		0.08	2.24			0.02	1.81		0.05	1.69
2.73		0.05	1.57		0.04	2.18			0.08	1.75		0.08	1.66
2.66		0.05	1.52		0.04	2.14			0.02	1.69		0.05	1.63
2.50		0.15	1.421		0.04	2.04			0.02	1.59		0.05	1.60
2.38		0.05	1.309		0.04	1.90			0.02	1.59		0.08	1.440
2.30		0.10				1.86			0.02	1.495		0.05	1.320
2.23		0.10				1.77			0.02	1.435		0.05	1.280
2.12		0.15				1.70			0.02	1.409		0.05	1.175
1.98	(5)	0.25				1.66			0.02	1.304		0.05	1.110
1.86		0.05				1.58			0.02	1.185		0.05	1.080
1.79		0.05				1.450			0.03			0.05	0.964
1.73		0.05				1.400							
656. K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O				661. KClO <sub>3</sub>		666. K <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·H <sub>2</sub> O		670. K <sub>4</sub> Fe(CN) <sub>6</sub>		674. K <sub>2</sub> SiF <sub>6</sub> *		678. KIO <sub>4</sub> *	
5.60	(10)	1.00		4.40	0.06	6.6	0.40	6.6	0.20	4.71	(62.5)	0.63	5.2
3.52	(10)	1.00		3.45	1.00	5.7	0.15	5.3	0.10	2.88		0.50	(50)
3.37	(10)	1.00		3.31	0.10	3.90	0.20	4.91	0.20	2.45		0.01	(125)
2.76		0.30		2.86	0.30	3.29	0.45	4.22	0.20	2.03		0.01	3.40
2.52		0.20		2.79	0.40	3.20	0.30	3.95	0.23	1.86		0.20	3.14
2.38		0.10		2.57	0.06	2.86	(20)	3.60	0.83	1.66		0.20	2.86
2.29		0.10		2.32	0.15	2.62		3.47	0.33	1.56		0.25	2.51
2.18		0.40		2.10	0.30	2.50		3.10	0.67	1.438		0.30	2.31
2.11		0.10		1.91	0.08	2.41		2.98	1.00	1.365		0.08	2.17
1.99		0.10		1.81	0.02	2.39	(9)	2.84	(30)	1.285		0.20	2.11
1.87		0.10		1.78	0.02	2.30		2.75	(25)	1.225		0.07	2.02
1.60		0.10		1.67	0.01	2.20	(20)	2.39		1.175		0.06	1.86
1.55		0.10		1.62	0.04	2.09		2.31		1.134		0.10	1.79
1.460		0.10		1.490	0.13	2.02		2.20		1.087		0.01	1.74
				1.421	0.02	2.00		2.12		1.056		0.01	1.70
				1.396	0.01	1.94		2.09		1.014		0.01	1.57
				1.330	0.01	1.86		2.02		0.996		0.02	1.52
657. KBrO <sub>3</sub> *				662. KClO <sub>4</sub> *		667. KCNO*		671. K <sub>4</sub> Fe(CN) <sub>6</sub> ·3H <sub>2</sub> O		675. KOH		679. KI*	
4.38	(10)	0.50		1.86	0.05	4.29	0.14	8.5	0.13	4.00		0.17	4.08
3.20	(20)	1.00		1.81	0.03	3.04	(25)	6.2	0.10	3.71		0.13	(25)
3.00	(12.5)	0.63		1.71	0.07	2.73	(50)	4.70	0.04	3.13		0.23	(62.5)
2.72		0.05		1.66	0.03	2.53	(15)	4.20	0.10B	2.93	(20)	0.67	(50)
2.18		0.50		1.61	0.03	2.30		3.90	0.05	2.69	(30)	1.00	
2.01		0.08		1.57	0.03	2.14		3.30	0.07	2.58		0.13	
1.89		0.25		1.52	0.03	1.92		2.92	0.15	2.44		0.17	
1.77		0.25		1.47	0.03	1.84		2.80	0.15	2.30		0.23	
1.73		0.10		1.42	0.03	1.77		2.60	0.15	2.14	(25)	0.83	
1.60		0.10		1.37	0.03	1.75		2.45	0.15	1.98		0.17	
1.50		0.10		1.32	0.03	1.68		2.35	0.15	1.83		0.17	
1.460		0.08		1.27	0.03	1.63		2.22	0.15	1.77		0.03	
1.412		0.25		1.22	0.03	1.52		2.15	0.15	1.73		0.03	
1.380		0.05		1.17	0.03	1.393		2.09	0.15	1.64		0.10	
1.358		0.15		1.12	0.03	1.358		2.03	0.15	1.55		0.07	
1.235		0.15		1.07	0.03	1.327		1.87	0.15	1.460		0.07	
1.178		0.10		1.02	0.03	1.298		1.83	0.15	1.400		0.07	
1.140		0.10		0.97	0.03	1.268		1.80	0.15	1.368		0.10	
1.100		0.05		0.92	0.03	1.191		1.68	0.15	1.340		0.07	
1.074		0.05		0.87	0.03	1.148		1.48	0.15	1.309			



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	(started patterns were checked with published crystal structure data)	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
680.	KMnO <sub>4</sub> *	685.	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	688.	K(C <sub>6</sub> H <sub>5</sub> OHSO <sub>3</sub> )	692.	K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O	696.	KH <sub>2</sub> PO <sub>2</sub>	700.	K <sub>2</sub> SeO <sub>4</sub>	
5.7	0.08	4.95	0.14	9.8	0.20	6.9	0.10	5.0	0.07	5.2	0.13	
4.55	0.50	4.53	0.03	5.2	0.15	6.2	0.13	3.65	(17.5)	0.58	4.30	
3.89	0.08	4.31	0.08	4.80	0.23	5.2	0.23	3.41	0.23	3.80	0.27	
3.71	0.30	4.05	0.20	4.29	0.05	4.85	0.38	3.26	(30)	1.00	3.08	
3.57	(30)	3.22	0.02	3.83	(40)	1.00	3.90	0.04	3.10	0.07	3.00	
3.43	0.04	3.10	0.08	3.38	0.20	3.74	0.05	2.61	(17.5)	0.58	2.59	
3.22	(50)	2.92	1.00	3.15	(15)	0.38	3.43	1.00	2.44	0.20	2.47	
2.95	(40)	2.80	0.14	2.98	(10)	0.25	3.08	0.30	2.30	0.17	2.35	
2.86	0.40	2.72	0.04	2.64	0.15	2.97	0.05	2.07	0.23	2.28	0.33	
2.56	0.30	2.62	0.35	2.52	0.15	2.87	0.25	1.97	0.30	2.15	0.33	
2.19	0.60	2.46	(30)	2.40	0.03	2.73	0.44	1.93	0.13	1.95	0.13	
2.03	0.02	2.32	(30)	2.32	0.03	2.56	(20)	1.86	0.20	1.90	0.20	
1.93	0.04	2.24	0.30	2.24	0.08	2.41	(25)	1.70	0.10	1.82	0.17	
1.84	0.20	2.14	0.12	2.13	0.03	2.30	0.20	1.61	0.13	1.74	0.27	
1.74	0.10	2.07	0.10	2.08	0.05	2.24	0.05	1.56	0.07	1.67	0.13	
1.68	0.08	2.02	0.25	2.03	0.05	2.14	0.08	1.480	0.03	1.61	0.17	
1.60	0.06	1.95	0.04	1.91	0.15	2.05	0.20	1.445	0.03	1.55	0.13	
1.54	0.02	1.91	0.30	1.69	0.03	1.99	0.08	1.400	0.03	1.498	0.17	
1.51	0.02	1.82	0.12	1.65	0.03	1.91	0.04	1.340	0.07	1.460	0.17	
1.480	0.04	1.77	0.06	1.57	0.03	1.86	0.03	1.290	0.07	1.415	0.03	
1.450	0.04a <sub>1</sub>	1.72	0.12	1.495	0.03	1.82	0.03	1.250	0.03B	1.397	0.10	
1.430	0.04	1.66	0.10	1.410	0.03	1.78	0.05	1.220	0.10	1.348	0.07	
1.391	0.04	1.62	0.02	1.320	0.03	1.75	0.04	1.185	0.03	1.310	0.03	
		1.57	0.16			1.71	0.10	1.130	0.03	1.280	0.07	
		1.53	0.04			1.67	0.03			1.252	0.07	
		1.50	0.02			1.57	0.04			1.200	0.07	
681.	K <sub>2</sub> MnO <sub>4</sub>	686.	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O*	689.	C <sub>6</sub> H <sub>5</sub> OK	693.	KH <sub>2</sub> PO <sub>4</sub> *	697.	C <sub>6</sub> H <sub>4</sub> (CO) <sub>2</sub> NK	701.	K <sub>2</sub> SeO <sub>3</sub>	
6.9	0.15	1.480	0.02	20.0	0.20							
5.6	0.10	1.451	0.04	17.0	(20) 1.00			14.5	(50) 1.00			
4.70	0.38	1.405	0.06	8.3	0.05	5.1	0.10	13.5	0.16	4.35	(6) 0.40B	
3.80	0.18	1.382	0.06	7.8	0.05	3.72	(50) 1.00	6.4	(12.5) 0.25	4.21	0.07B	
3.40	0.44	1.330	0.07	7.1	0.15	3.00	0.08	5.6	0.02	3.69	0.07	
3.17	(40) 1.00	1.298	0.02	6.2	0.15	2.90	(50) 1.00	4.91	0.08	3.08	(15) 1.00B	
3.03	(20) 0.50	1.275	0.10	5.3	(10) 0.50	2.63	0.16	4.35	0.04	2.94	(4) 0.27B	
2.92	0.50	1.238	0.08	4.51	(20) 1.00	2.53	0.06	3.59	0.04	2.85	0.20	
2.77	0.03	1.203	0.02	4.29	0.05	2.34	0.12	3.45	0.02	2.63	0.13	
2.66	0.03	1.176	0.08	4.01	0.05	2.22	0.03	3.30	0.16	2.37	0.07	
2.26	(25) 0.63	1.135	0.04	3.90	0.05	1.95	(20) 0.40	3.09	(12.5) 0.25	2.30	0.13	
2.03	0.15	1.120	0.04	3.80	0.05	1.90	0.02	2.90	0.08	2.20	0.13	
1.97	0.31			3.61	0.08	1.66	0.06	2.67	0.04	2.10	0.13	
1.87	0.10			3.43	0.08	1.57	0.08	2.55	0.02	2.03	0.07	
1.79	0.20			3.27	0.50	1.450	0.04	2.35	0.02	1.97	0.07	
1.73	0.15	4.97	0.28	2.98	0.05	1.345	0.06	2.17	0.02	1.92	0.07	
1.69	0.15	4.33	0.13	2.87	0.35	1.318	0.02	2.07	0.02	1.84	0.07	
1.58	0.15	4.07	0.16	2.80	0.40	1.270	0.04	1.87	0.02	1.79	0.07	
1.52	0.10	3.23	0.02	2.66	0.08	1.200	0.06	1.77	0.02	1.73	0.07	
1.455	0.23	3.08	(20) 0.32	2.59	0.08	1.175	0.02	1.68	0.02	1.67	0.07	
1.385	0.10	2.95	(20) 0.32	2.55	0.05	1.008	0.02			1.62	0.07	
1.330	0.10	2.81	0.32	2.47	0.05					1.57	0.07	
1.295	0.05	2.74	0.13	2.39	0.05					1.53	0.07	
1.265	0.10	2.60	0.24	2.30	0.05					1.398	0.07	
1.210	0.05	2.45	(62.5) 1.00	2.25	0.05					1.373	0.07	
1.130	0.05	2.32	0.06	2.19	0.30					1.341	0.07	
		2.27	0.13							1.316	0.07	
		2.16	0.10							1.180	0.07	
		2.07	0.13									
		2.02	0.16									
682.	KNO <sub>2</sub> *	687.	KHC <sub>2</sub> O <sub>4</sub> ·1/2H <sub>2</sub> O	690.	K <sub>3</sub> PO <sub>4</sub>	694.	Potassium Ammonium Phosphate	698.	C <sub>6</sub> H <sub>4</sub> COOH·COOK	702.	KSeCN	
4.66	0.12	6.1	0.08	5.5	0.30	5.6	0.40	13.4	(30) 1.00	4.97	0.07	
3.77	(25) 1.00	4.83	0.12	3.65	0.30	5.0	0.53	4.99	(20) 0.67	4.42	0.17	
3.03	(9) 0.36	4.42	0.12	3.44	0.04	3.75	(12.5) 0.83	4.20	0.23	4.05	0.33	
2.77	0.08	3.91	0.04	3.15	0.30	3.30	0.40	4.03	0.23	3.70	0.50	
2.66	(7) 0.28	3.44	0.03	3.03	(50) 1.00	2.91	1.00	3.70	0.17	3.43	0.20	
2.19	0.24	3.31	0.02	2.75	(30) 0.60	2.65	0.33	3.43	0.05	3.33	0.17	
2.06	0.08	3.12	1.00	2.56	(25) 0.50	2.56	0.53	3.14	0.20	3.14	0.20	
1.96	0.12	2.96	0.02	2.45	0.20	2.33	0.20	2.99	(15) 0.50	2.99	0.17	
1.76	0.04	2.78	0.40	2.39	0.40	2.10	0.07	2.89	0.07	2.79	0.07	
1.54	0.04	2.65	0.02	2.23	0.16	1.95	(12.5) 0.83	2.70	0.03	2.70	0.03	
1.365	0.04	2.57	0.08	2.13	0.04	1.87	0.07	2.64	0.20	2.64	0.20	
		2.43	0.20	2.07	0.04	1.69	0.07B	2.51	0.07	2.51	0.07	
		2.35	0.14	1.93	0.12	1.57	0.20	2.39	0.13	2.39	0.13	
		2.21	0.08	1.89	0.02	1.450	0.13	2.25	0.10	2.25	0.10	
		2.14	0.02	1.82	0.20	1.345	0.13	2.15	0.03	2.15	0.03	
		2.06	0.03	1.77	0.04	1.270	0.07	2.06	0.03	2.06	0.03	
		2.02	0.03	1.73	0.02	1.200	0.13	2.01	0.03	2.01	0.03	
		2.00	0.03	1.68	0.02	1.070	0.07	1.96	0.03	1.96	0.03	
		1.93	0.03	1.64	0.18			1.88	0.03	1.88	0.03	
		1.89	0.03	1.58	0.02			1.83	0.03	1.83	0.03	
		1.82	0.04	1.52	0.02			1.78	0.03	1.78	0.03	
		1.77	0.02	1.462	0.02							
		1.73	0.02	1.435	0.02							
		1.68	0.02	1.407	0.06							
		1.64	0.02	1.370	0.04							
		1.61	0.02									
		1.57	0.02									
		1.53	0.02									
		1.49	0.02									
		1.45	0.02									
		1.41	0.02									
		1.37	0.02									
		1.33	0.02									
		1.29	0.02									
		1.25	0.02									
		1.21	0.02									
		1.17	0.02									
		1.13	0.02									
		1.09	0.02									
		1.05	0.02									
		1.01	0.02									
		0.97	0.02									
		0.93	0.02									
		0.89	0.02									
		0.85	0.02									
		0.81	0.02									
		0.77	0.02									
		0.73	0.02									
		0.69	0.02									
		0.65	0.02									
		0.61	0.02									
		0.57	0.02									
		0.53	0.02									
		0.49	0.02									
		0.45	0.02									
		0.41	0.02									
		0.37	0.02									
		0.33	0.02									
		0.29	0.02									
		0.25	0.02									
		0.21	0.02									
		0.17	0.02									
		0.13	0.02									
		0.09	0.02									
		0.05	0.02									
		0.01	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									
		0.00	0.02									



(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
703. KAlSi <sub>3</sub> O <sub>8</sub>		706. K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>		710. K <sub>2</sub> SO <sub>3</sub> ·2H <sub>2</sub> O		714. Potassium Guaiacol Sulfonate		719. KH(C <sub>6</sub> H <sub>4</sub> O <sub>6</sub> )		723. 3K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ·H <sub>2</sub> O	
4.24 (15) 0.38	4.88	0.12	4.13	0.20	9.8	0.10	6.3	0.05	5.1	0.16	
4.01 0.20	3.72	0.24	3.47	0.16	6.7	0.25	5.4	0.05	4.73	(6) 0.48	
3.85 0.20	3.45	0.24	2.96	(50) 1.00	5.7	1.00	4.87	0.05	4.24	0.32	
3.69 0.20	3.24	(125) 1.00	2.87	(40) 0.80	4.43	0.35	4.36	0.03	3.93	0.16	
3.49 0.15	3.03	0.08	2.40	0.16	4.10	1.00	4.10	0.03	3.73	0.08	
3.35 (10) 0.25	2.73	0.12	2.06	(40) 0.80	3.71	(20) 1.00	3.80	0.25	3.62	0.08	
3.25 (40) 1.00	2.64	0.08	1.94	0.04	3.42	0.10	3.64	(30) 0.75	3.48	(8) 0.64	
3.03 0.13	2.55	0.05	1.88	0.02	3.27	0.30	3.22	(30) 0.75	3.35	0.16	
2.94 0.25	2.47	0.20	1.69	0.25	3.12	0.75	2.87	0.75	3.19	(12.5) 1.00	
2.88 0.08	2.42	0.01	1.64	0.12	2.94	0.20	2.63	0.15	3.04	0.48	
2.76 0.10	2.29	0.03	1.475	0.18	2.68	0.40	2.46	(40) 1.00	2.95	0.08	
2.61 0.15	2.16	0.02	1.440	0.08	2.50	0.35	2.38	0.20	2.83	0.48	
2.52 0.13	2.10	0.10	1.315	0.10	2.43	0.30	2.34	0.10	2.73	0.48	
2.43 0.13	1.99	0.06	1.295	0.10	2.38	0.05	2.28	0.03	2.64	0.40	
2.33 0.08	1.93	0.10	1.200	0.04	2.38	0.10	2.22	0.15	2.57	0.16	
2.16 0.25	1.87	0.03	1.115	0.08	2.23	0.15	2.17	0.03	2.48	0.16	
2.10 0.03	1.81	0.08	1.078	0.04	2.18	0.10	2.10	0.20	2.40	0.08	
2.02 0.03	1.76	0.01	0.985	0.02	2.12	0.20	2.02	0.03	2.37	0.08	
1.98 0.10	1.72	0.03	0.958	0.02	2.03	0.10	1.98	0.08	2.24	0.08	
1.92 0.10	1.62	0.12		1.97	1.92	0.10	1.90	0.10	2.19	0.16	
1.85 0.03	1.58	0.06		1.92	1.86	0.08	1.85	0.10	2.15	0.08	
1.80 0.25	1.52	0.02	711. KHSO <sub>4</sub>	1.86	1.82	0.10	1.78	0.13	2.11	0.16	
1.73 0.05	1.427	0.06	5.1	1.82	1.79	0.08	1.74	0.03	2.03	0.16	
1.65 0.03	1.404	0.01	4.56	1.79	1.74	0.05	1.71	0.03	2.00	0.16	
1.61 0.03	1.371	0.01	4.19	1.74			1.68	0.03	1.96	0.16	
1.57 0.03	1.336	0.02	3.90				1.63	0.03	1.84	0.24	
1.54 0.03			3.78								
1.51 0.05			3.67								
1.468 0.10			3.50								
			0.28								
			0.04								
			0.04								
			0.28								
			0.06								
			0.06								
			1.00								
			0.60								
			0.32								
			0.12								
			0.04								
			0.08								
			0.06								
			0.20								
			0.24								
			0.12								
			0.04								
			0.08								
			0.06								
			0.20								
			0.24								
			0.12								
			0.06								
			0.16								
			0.32								
			0.06								
			0.04								
			0.06								
			0.06								
			0.08								
			4.75								
			4.55								
			3.65								
			3.09								
			2.95								
			2.83								
			2.70								
			2.57								
			2.45								
			2.33								
			2.27								
			2.13								
			2.02								
			1.97								
			1.92								
			1.87								
			1.82								
			1.78								
			1.73								
			1.70								
			1.67								
			1.63								
			1.61								
			1.54								
			1.51								
			1.480								
			1.439								
			1.422								
			1.388								
			1.352								
			1.321								
			1.301								
			1.278								
			1.252								
			1.228								
			1.190								
			1.162								



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
729. KVO <sub>3</sub>		736. RbNO <sub>3</sub> *		740. Se*		744. SiC (commercial)*		748. Ag <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>		752. Ag <sub>2</sub> CO <sub>3</sub>	
5.3	0.16	4.28	0.20	3.78	(5) 0.33			10.0	(62.5) 1.00	4.77	0.20
3.90	0.08	3.85	(7) 0.35	3.02	(15) 1.00	2.63	0.20	4.11	0.03	4.31	0.20
3.71	0.06	3.29	0.05	2.18	0.27	2.59	0.06	3.93	0.03	3.05	0.04
3.11	(62.5) 1.00	3.02	(20) 1.00	2.07	(6) 0.40	2.51	(50) 1.00	3.70	0.10	2.73	(50) 0.50
2.82	(20) 0.32	2.89	0.20	2.00	0.33	2.36	0.40	3.31	0.10	2.65	(100) 1.00
2.60	(12.5) 0.20	2.71	(5) 0.25	1.77	0.27	2.17	0.12	3.04	(50) 0.80	2.55	0.02
2.43	0.11	2.46	0.25	1.64	0.20	2.08	0.02	2.91	(10) 0.16	2.48	0.01
2.30	0.09	2.35	0.05	1.51	0.27	2.00	0.04	2.77	0.08	2.42	0.15
1.95	0.06	2.23	0.15	1.430	0.20	1.83	0.02	2.68	0.14	2.37	0.03
1.89	0.02	2.13	0.10	1.320	0.13	1.68	0.04	2.59	0.06	2.32	0.04
1.77	0.03	1.98	0.05	1.239	0.07	1.60	0.02	2.48	0.06	2.27	(30) 0.30
1.69	0.11	1.90	0.25	1.180	0.07	1.54	(40) 0.80	2.33	0.13	2.20	0.01
1.57	0.05B	1.86	0.05	1.125	0.07	1.420	0.16	2.21	0.10	2.15	0.08
1.50	0.02	1.82	0.05	1.084	0.13	1.312	(30) 0.60	2.04	0.06	2.03	0.08
1.455	0.05	1.74	0.20	1.038	0.07	1.285	0.04	1.98	0.06	1.92	0.08
1.420	0.03	1.70	0.05			1.257	0.04	1.85	0.06	1.86	0.04
1.310	0.03	1.51	0.05	741. H <sub>2</sub> SeO		1.220	0.02	1.80	0.03	1.77	0.10
1.245	0.02	1.424	0.10			1.178	0.02	1.74	0.03	1.67	0.08
1.170	0.02	1.351	0.10			1.134	0.02	1.69	0.02	1.63	0.10
1.087	0.02	1.320	0.05	8.1	0.29	1.110	0.02	1.65	0.03	1.59	0.07
		1.288	0.10	7.2	0.29	1.089	0.06	1.57	0.02	1.53	0.03
730. KS <sub>2</sub> COC <sub>2</sub> H <sub>5</sub>		1.187	0.05	6.3	0.29	1.044	0.08	1.53	0.02	1.50	0.02
7.5	(8) 1.00	1.145	0.10	4.55	(4) 0.57	0.999	0.14	1.50	0.02	1.462	0.01
3.60	(7) 0.88			4.22	0.29	0.990	0.04			1.440	0.05
3.22	(6) 0.75	737. Rb <sub>2</sub> SO <sub>4</sub> *		3.90	0.57	0.974	0.08	749. Ag <sub>3</sub> AsO <sub>4</sub> *		1.398	0.04
3.10	0.50	3.49	0.20	3.60	(7) 1.00	0.958	0.02			1.370	0.13
2.95	0.13	3.26	0.05	3.39	0.43	0.944	0.04	3.07	0.17	1.328	0.04
2.67	0.13B	3.10	(15) 0.75	2.98	(5) 0.71	0.912	0.02	2.74	(75) 1.00	1.300	0.02
2.50	0.38	2.98	(20) 1.00	2.61	0.29	0.901	0.02	2.50	(50) 0.67	1.222	0.03
2.41	0.25	2.60	0.10	2.45	0.43	0.890	0.16	1.94	0.05	1.133	0.03
2.33	0.13	2.51	0.15	2.38	0.29	0.865	0.08	1.77	0.13		
2.27	0.25	2.45	0.10	2.25	0.29	0.839	0.12	1.70	0.33	753. AgClO <sub>4</sub> ·H <sub>2</sub> O	
2.19	0.25	2.29	0.15	2.12	0.43	0.805	0.02	1.63	(40) 0.53	6.9	0.20
		2.16	(10) 0.50	2.08	0.14	0.771	0.04	1.53	0.20	5.2	0.20
731. Re*		2.07	0.08	2.03	0.14	0.738	0.10	1.369	0.13	4.02	0.50
2.38	(10) 0.33	2.00	0.05	2.00	0.14	0.727	0.02	1.335	0.23	3.78	0.04
2.22	(6) 0.20	1.95	0.10	1.96	0.43			1.305	0.11	3.50	(50) 1.00
2.10	(30) 1.00	1.91	0.08	1.90	0.43	745. SiO <sub>2</sub> * (α-cristobalite)		1.137	0.20	3.39	(40) 0.80
1.62	0.10	1.83	0.05	1.86	0.43			1.118	0.12	3.11	0.16
1.379	0.17	1.75	0.15	1.82	0.43	4.04	(125) 1.00	1.082	0.11	2.95	0.02
1.260	0.13	1.66	0.05	1.72	0.43	3.13	0.16	1.021	0.07	2.77	(40) 0.80
1.170	0.17	1.63	0.05	1.63	0.29	2.85	(25) 0.20	0.994	0.09	2.49	0.14
1.151	0.17	1.58	0.05	1.60	0.14	2.48	(40) 0.32	0.915	0.05	2.42	0.60
0.928	0.03	1.488	0.10	1.50	0.29	2.11	0.05			2.25	0.02
0.884	0.07	1.440	0.05			2.02	0.05	750. AgBrO <sub>3</sub> *		2.19	0.02
0.868	0.03	1.400	0.10	742. Si*		1.93	0.12	3.48	0.13	2.10	0.30
		1.345	0.10			1.87	0.12	(20) 0.27	2.04	0.12	
				3.12	(100) 1.00	1.69	0.05	3.04	1.99	0.30	
732. Rh*				1.91	(100) 1.00	1.61	0.12	2.95	(75) 1.00	1.95	0.12
2.20	(100) 1.00	738. RbAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O*		1.63	(62.5) 0.63	1.57	0.01	2.70	0.03	1.82	0.02
1.90	(50) 0.50	5.5	0.27	1.354	0.18	1.53	0.04	2.58	0.01	1.78	0.04
1.345	0.30	5.0	0.10	1.242	0.25	1.494	0.06	2.28	0.02	1.76	0.10
1.146	(40) 0.40	4.34	(30) 1.00	1.104	0.40	1.430	0.05	2.22	0.08	1.70	0.04
1.099	0.13	4.09	0.23	0.958	0.06	1.400	0.02	2.15	0.20	1.66	0.04
0.952	0.04	3.28	(15) 0.50	0.916	0.13	1.370	0.03	2.02	0.05	1.61	0.04
0.873	0.15	3.07	0.33	0.857	0.08	1.339	0.03	1.92	0.05	1.56	0.10
0.852	0.15	2.81	(20) 0.67	0.826	0.03	1.300	0.03	1.79	0.07	1.52	0.04
0.777	0.08	2.73	0.13	0.782	0.01	1.279	0.03	1.74	(20) 0.27	1.422	0.14
0.733	0.10	2.62	0.13	0.760	0.04α <sub>1</sub>	1.235	0.01	1.69	0.11	1.390	0.12
		2.50	0.23	0.724	0.06α <sub>1</sub>	1.203	0.01	1.65	0.01	1.350	0.03
		2.36	0.23	0.705	0.04α <sub>1</sub>	1.181	0.02	1.56	0.03		
733. RbBr*		2.26	0.03			1.095	0.03	1.52	0.03		
3.43	(17.5) 1.00	2.16	0.03	743. SiC*				1.490	0.01	754. AgCl*	
2.42	(10) 0.57	2.04	0.17	2.51	(100) 1.00	746. SiO <sub>2</sub> * (α-quartz)		1.470	0.03	3.20	(40) 0.40
1.97	0.17	1.99	0.03	2.17	0.20			1.450	0.03	2.77	(100) 1.00
1.71	0.11	1.94	0.33	1.54	(62.5) 0.63	4.25	(25) 0.25	1.411	0.01	1.96	(75) 0.75
1.53	(6) 0.34	1.87	0.13	1.310	(50) 0.50	3.35	(100) 1.00	1.390	0.01	1.67	0.20
1.400	0.23	1.70	0.13	1.255	0.05	2.45	0.15	1.358	0.05	1.60	0.25
1.143	0.11	1.64	0.27	1.087	0.06	2.29	0.10			1.385	0.09
		1.488	0.20	0.998	0.18	2.23	0.06	751. AgBr*		1.270	0.06
		1.448	0.07	0.972	0.06	2.12	0.09	2.88	(50) 1.00	1.240	0.20
734. RbCl*		1.410	0.03	0.887	0.13	1.97	0.08	2.03	(30) 0.60	1.131	0.13
3.80	(3) 0.17	1.365	0.03	0.837	0.10	1.82	(25) 0.25	1.66	(10) 0.20	1.065	0.01
3.29	(17.5) 1.00	1.332	0.03	0.768	0.02	1.66	0.08	1.441	0.08	0.980	0.01
2.32	(10) 0.57	1.305	0.03	0.735	0.06	1.54	0.20	1.320	0.02	0.937	0.01
1.98	0.11	1.201	0.13	0.724	0.02	1.450	0.02	1.289	0.20	0.924	0.04
1.89	0.17			0.688	0.03	1.375	0.25	1.178	0.12	0.877	0.01
1.64	0.11	739. Ru*		0.663	0.01	1.299	0.04	1.019	0.02	0.836	0.01
1.50	0.06	2.33	(40) 0.40			1.256	0.03	0.963	0.02α <sub>1</sub>		
1.468	0.17	2.13	(30) 0.30			1.228	0.03	0.913	0.02α <sub>1</sub>		
1.340	0.11	2.04	(100) 1.00			1.200	0.06	0.871	0.02α <sub>1</sub>		
1.095	0.06	1.57	0.25			1.180	0.08				
		1.345	0.25			1.155	0.01				
		1.213	0.30			1.080	0.04				
735. RbI*		1.165	0.04			1.048	0.02				
4.24	0.04	1.140	0.30			1.035	0.01				
3.66	(25) 1.00	1.128	0.15			1.015	0.01				
2.58	(20) 0.80	1.069	0.03			747. Ag*		2.36	(75) 1.00		
2.20	0.04	1.025	0.04			2.04	(40) 0.53				
2.11	0.20	0.971	0.04			1.445	0.27				
1.83	0.15	0.905	0.10α <sub>1</sub>			1.232	(40) 0.53				
1.63	(8) 0.32	0.884	0.02			1.179	0.05				
1.493	0.16	0.867	0.20α <sub>1</sub>			1.022	0.01				
1.292	0.04	0.839	0.10α <sub>1</sub>			0.938	0.08α <sub>1</sub>				
1.220	0.08	0.818	0.04α <sub>1</sub>			0.915	0.05α <sub>1</sub>				
1.157	0.04	0.803	0.06α <sub>1</sub>			0.834	0.03α <sub>1</sub>				
1.103	0.04	0.790	0.02			0.786	0.04α <sub>1</sub>				
		0.780	0.04α <sub>1</sub>			0.691	0.03α <sub>1</sub>				
		0.751	0.15α <sub>1</sub>								
		0.733	0.06α <sub>1</sub>								
		0.691	0.04α <sub>1</sub>								
		0.682	0.04								
		0.677	0.04α <sub>1</sub>								



(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	
755. Ag <sub>2</sub> CrO <sub>4</sub>		758. Silver Potassium Cyanide		762. AgNO <sub>3</sub> *		766. Ag <sub>2</sub> SO <sub>4</sub> *		769. Ag <sub>3</sub> V <sub>2</sub> O <sub>7</sub>		774. NaNH <sub>2</sub>				
7.0	0.06			4.51	(20)	0.50	4.71	0.07	4.6	0.10	5.7	0.27		
6.5	0.06	9.0	0.30	4.08	(20)	0.50	3.98	0.27	2.88	(150)	1.00	5.2	(10)	0.67
6.0	0.06	6.2	0.30	3.66		0.38	3.17	0.53	2.77	(150)	1.00	3.40		0.07
5.6	0.08	4.40	(25)	0.50	3.00	(40)	1.00	2.86	(75)	1.00	0.20	3.20	(8)	0.53
4.97	0.04	3.43	(50)	1.00	2.80		0.38	2.64	(40)	0.53	0.20	3.00		0.40
4.49	0.04	3.18	(40)	0.80	2.73		0.44	2.52		0.11	0.13	2.85		0.53
4.12	0.04	3.02		0.02	2.53		0.38	2.41		0.33	0.10	2.69		0.13
3.84	0.04	2.82		0.40	2.29		0.31	2.35		0.01	0.01	2.65		0.27
3.49	0.08	2.61		0.06	2.24		0.25	2.27		0.08	0.01	2.35	(15)	1.00
3.14	(50)	2.38		0.40	2.15		0.15	1.97		0.11	0.05	2.24		0.27
3.02	(17.5)	0.35	2.31	0.30	2.11		0.10	1.91		0.40	0.20	2.18		0.13
2.92	(15)	0.30	2.21	0.12	2.08		0.50	1.75		0.03	0.13	2.05		0.07
2.85		0.30	2.13	0.02	1.96		0.18	1.70		0.13	0.03	2.02		0.07
2.65		0.30	2.07	0.20	1.90		0.10	1.66		0.09	0.01	1.97		0.40
2.47		0.30	1.99	0.20	1.83		0.25	1.64		0.07	0.01	1.91		0.07
2.31		0.06	1.85	0.16	1.70		0.15	1.58		0.01	0.04	1.83		0.07
2.23		0.08	1.81	0.08	1.66		0.15	1.56		0.09	0.13	1.75		0.13
2.14		0.06	1.76	0.04	1.57		0.05	1.53		0.09	0.10	1.70		0.20
2.07		0.06	1.71	0.40	1.490		0.10	1.465		0.05	0.10	1.66		0.13
1.95		0.30	1.67	0.12	1.420		0.08	1.447		0.07	0.01	1.66		0.07
1.84		0.20	1.59	0.16	1.382		0.05	1.400		0.07	0.01	1.495		0.07
1.79		0.08	1.55	0.08	1.340		0.13	1.361		0.01	0.01	1.460		0.07
1.77		0.08	1.50	0.02	1.310		0.03	1.330		0.11	0.01			
1.72		0.16	1.465	0.08				1.270		0.04	0.01			
1.66		0.06	1.422	0.12				1.230		0.05	0.01			
1.61		0.08	1.385	0.02	763. AgNO <sub>3</sub> *			1.187		0.01	0.01	5.9	(20)	1.00
1.55		0.08	1.190	0.02	3.95	(50)	0.67	1.161		0.04		5.3		0.10
1.53		0.02	1.050	0.02	3.06	(75)	1.00	1.112		0.03		4.62	(9)	0.45
1.50		0.02			2.90		0.13	1.091		0.04		4.08		0.30
1.470		0.08			2.58		0.40	1.075		0.03		3.70		0.25
1.430		0.06			2.11		0.40					3.41		0.15
1.394		0.06			1.97	(50)	0.67					3.21	(20)	1.00
1.325		0.04	3.74	(40)	1.00		0.13	767. Ag <sub>2</sub> S*				2.98		0.40
1.268		0.04	2.29	(30)	0.75		0.07	3.94	0.02			2.84		0.40
1.230		0.04	1.95	(15)	0.40		0.07	3.42	0.12			2.72		0.10
		0.04	1.62		0.05		0.07	3.07	0.20			2.64		0.05
		0.04	1.485		0.08		0.03	2.80	0.30			2.52		0.30
			1.321		0.08		0.07	2.59	0.80B			2.35		0.30
			1.247		0.05		0.07	2.43	(40)			2.26		0.30
			1.145		0.03		0.05	2.37	(50)			2.09		0.05
			1.096		0.03		0.03	2.19				2.02		0.15
							0.07	2.07	(20)			1.98		0.05
							1.292	1.98				1.79		0.15
							1.192	1.96				1.72		0.10B
								1.90				1.62		0.15
								1.86				1.56		0.05
								1.81						
								1.77						
								1.71						
								1.58						
								1.54						
								1.51						
								1.470						
								1.455						
								1.407						
								1.336						
													</	



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
778. Sodium Asparaginate		783. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O		787. NaBrO <sub>3</sub> *		792. Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O		796. NaKCO <sub>3</sub>		800. NaCl*	
5.5	0.25	9.1	0.07	4.75	0.40	5.3	0.31	3.07	(30) 0.48	3.25	0.05
4.20	(8) 1.00	8.0	0.07	3.86	0.27	4.15	0.08	2.72	(62.5) 1.00	2.81	(150) 1.00
3.82	(4) 0.50	7.1	0.13	3.34	0.13	2.76	1.00	2.63	0.16	1.99	(125) 0.83
3.60	0.25	5.7	0.20	2.99	(15) 1.00	2.67	(17.5) 0.44	2.57	0.16	1.70	0.02
3.09	0.13	5.2	0.13	2.73	(8) 0.53	2.55	0.03	2.48	0.16	1.63	(50) 0.33
2.91	0.25	4.86	(7) 0.47	2.23	0.20	2.47	0.25	2.36	0.08	1.410	0.13
2.69	(4) 0.50	4.45	0.07	2.11	0.07	2.37	(25) 0.63	2.24	0.40	1.293	0.01
2.46	0.25	3.96	0.40	2.01	0.20	2.24	0.20	2.21	0.40	1.260	0.33
2.26	0.13	3.61	0.07	1.93	0.07	2.18	0.15	2.14	0.03	1.150	0.20
2.16	0.13	2.97	0.20	1.85	(12.5) 0.83	2.12	0.03	1.93	0.14	1.080	0.01
2.02	0.50	2.84	(8) 0.53	1.78	0.07	2.06	0.18	1.88	0.14	0.997	0.30
		2.57	(15) 1.00	1.62	0.07	2.00	0.31	1.81	0.10	0.941	0.05 <sub>α1</sub>
		2.46	0.07	1.57	0.07	1.91	0.08	1.78	0.10	0.892	0.03 <sub>α1</sub>
		2.34	0.20	1.53	0.20	1.78	0.08	1.73	0.05	0.852	0.03 <sub>α1</sub>
779. NaN <sub>3</sub> *		2.20	0.07	1.495	0.07	1.74	0.08	1.59	0.06	0.813	0.01
3.09	0.10	2.14	0.07	1.460	0.27	1.67	0.08B	1.57	0.13	0.782	0.01
2.91	(125) 1.00	2.08	0.07	1.313	0.27	1.65	0.08	1.53	0.10	0.755	0.01 <sub>α1</sub>
2.42	(25) 0.20	2.02	0.07	1.287	0.07	1.61	0.25	1.362	0.16		
2.18	(50) 0.16	1.95	0.07	1.245	0.13	1.54	0.05	1.287	0.02		
1.82	0.05	1.90	0.13	1.220	0.07	1.470	0.03	1.230	0.02		
1.78	0.02	1.85	0.13	1.110	0.07	1.431	0.05	1.211	0.02	801. Na <sub>2</sub> CrO <sub>4</sub> *	
1.70	0.02	1.78	0.07	1.082	0.07	1.380	0.03	1.170	0.02	4.97	0.11
1.63	0.02	1.75	0.10	1.042	0.13	1.345	0.03	1.030	0.05	4.09	(30) 0.48
1.54	0.10	1.70	0.10			1.315	0.08			3.88	0.48
1.478	0.02	1.65	0.07	788. NaBr*						3.59	0.32
1.455	0.02	1.61	0.07							2.91	(62.5) 1.00
1.400	0.02			3.44	(9) 0.45	793. Na <sub>2</sub> CO <sub>3</sub> ·2½H <sub>2</sub> O		797. NaClO <sub>3</sub> *		2.73	(40) 0.64
1.367	0.04	784. Na <sub>3</sub> (B <sub>3</sub> O <sub>6</sub> )*		2.96	(20) 1.00	10.0	0.15	4.65	0.20	2.48	0.24
1.270	0.02	6.9	0.04	2.09	(12.5) 0.63	4.90	0.15	3.79	0.33	2.17	0.10
1.240	0.02	6.6	0.08	1.79	0.20	3.17	0.15	3.28	0.67	2.12	0.05
1.212	0.01	6.0	0.04	1.71	0.20	3.05	(17.5) 0.88	2.94	1.00	2.03	0.20
1.176	0.06	6.0	0.04	1.487	0.10	2.75	0.30	2.68	0.40	1.94	0.16
1.140	0.02	5.3	0.32	1.362	0.05	2.64	(20) 1.00	2.32	0.01	1.79	0.24
1.052	0.02	4.77	(15) 0.60	1.329	0.35	2.48	0.10	2.18	0.33	1.71	0.02
1.039	0.02	4.35	0.04	1.216	0.10	2.43	(10) 0.50	2.07	0.07	1.68	0.03
1.029	0.01	4.20	0.04	1.145	0.05	2.35	0.10	1.98	0.13	1.65	0.05
		3.72	0.24	1.053	0.05	2.24	0.25	1.89	0.01	1.62	0.20
		3.44	0.40			2.02	0.15	1.83	0.07	1.50	0.20
780. Sodium Barbitol		3.30	0.04	789. CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COONa		1.77	0.05	1.76	(50) 0.67	1.465	0.03
8.6	(25) 1.00	3.00	0.04	14.5	(62.5) 1.00	1.73	0.10	1.64	0.01	1.417	0.08
6.0	(10) 0.40	2.85	(25) 1.00	5.1	0.02	1.65	0.10	1.59	0.11	1.370	0.06
5.4	0.32	2.75	0.08	3.75	(4) 0.06	1.59	0.10	1.55	0.03	1.340	0.03
4.25	(12.5) 0.50	2.64	(20) 0.80	3.52	0.03	1.320	0.05	1.51	0.11	1.270	0.02
3.35	0.24	2.51	0.20	3.10	0.02			1.470	0.03	1.210	0.10
3.13	0.16	2.38	0.12	3.00	0.02	794. Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O		1.434	0.13	1.170	0.03
2.99	0.04	2.33	0.32	2.80	(4) 0.06	5.3	(10) 0.57	1.404	0.01		
2.83	0.12	2.24	0.20	1.76	0.02	4.50	0.23	1.317	0.01	802. Na <sub>2</sub> CrO <sub>4</sub> ·4H <sub>2</sub> O	
2.66	0.04	2.18	0.20			4.03	(6) 0.34	1.289	0.03	6.0	0.33
2.52	0.04	2.11	0.04			3.52	0.11	1.264	0.05	5.2	0.50
2.38	0.04	2.01	0.28			3.44	0.11	1.222	0.05	4.50	(30) 1.00
2.22	0.04	1.88	0.40			3.24	0.09	1.200	0.05	3.70	0.20
2.03	0.04	1.82	0.16			3.17	0.09	1.145	0.03	3.58	(20) 0.67
		1.75	0.20	790. (CH <sub>3</sub> ) <sub>2</sub> AsO <sub>3</sub> ·ONa·3H <sub>2</sub> O		3.01	0.23	1.130	0.01	3.20	(20) 0.67
		1.66	0.16	6.0	(7) 0.78	2.89	(17.5) 1.00	1.114	0.03	2.98	0.58
		1.61	0.24	5.5	0.55	2.80	0.34	1.094	0.01	2.86	0.50
781. NaBiO <sub>3</sub>				5.1	0.33	2.67	0.17	1.068	0.03	2.71	0.20
15.6	0.33	785. NaBO <sub>3</sub> ·2H <sub>2</sub> O		4.30	(9) 1.00	2.57	0.23	1.042	0.01	2.66	0.33
7.5	1.00	5.4	(8) 1.00	4.11	0.66	2.43	0.34	1.028	0.08	2.53	0.07
4.9	0.33	4.70	0.13	3.57	(8) 0.89	2.36	0.06			2.44	0.10
4.06	(4) 0.67	3.96	0.13	3.22	0.11	2.29	0.11	798. NaClO <sub>4</sub> *		2.25	0.20
3.74	0.17	3.03	(8) 1.00	3.10	0.33	2.22	0.06	4.79	0.08	2.10	0.20
2.95	0.25	2.71	(6) 0.75	2.98	0.11	2.16	0.06	3.97	(40) 0.53	2.03	0.20
2.80	0.33	2.62	0.13	2.84	0.66	2.10	0.09	3.53	(75) 1.00	1.93	0.23
2.62	(4) 0.67	2.44	0.17	2.74	0.11	2.05	0.06	3.25	0.07	1.86	0.13
2.44	0.17	2.37	0.25	2.51	0.22	1.98	0.17	2.95	(40) 0.53	1.79	0.13
2.33	0.17	2.20	0.13	2.39	0.11	1.94	0.09	2.85	0.17	1.73	0.07
2.23	0.25	2.13	0.38	2.28	0.11	1.91	0.09	2.50	0.04	1.70	0.03
2.03	0.17	2.01	0.13	2.14	0.44	1.85	0.06	2.39	0.40	1.65	0.03
1.85	0.33	1.87	0.13	2.04	0.33	1.79	0.09	2.27	0.17	1.58	0.20
1.78	0.17	1.81	0.13	1.81	0.33	1.75	0.09	2.12	0.05	1.480	0.10
1.61	0.17	1.74	0.13	1.73	0.22			2.07	0.04	1.395	0.03
1.58	0.17	1.70	0.13	1.69	0.11	795. NaHCO <sub>3</sub> *		1.98	0.07	1.335	0.03
1.54	0.17	1.64	0.13	1.65	0.11			1.90	0.33	1.210	0.07
1.480	0.33	1.51	0.13	1.61	0.22	3.49	(2) 0.16	1.77	0.13		
1.310	0.17			1.53	0.11	3.04	0.16	1.68	0.20	803. Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
1.257	0.17	786. Sodium Borobenzoate		1.425	0.22	2.94	(12.5) 1.00	1.62	0.01	5.7	0.20
1.215	0.17	4.40	(5) 0.83	1.355	0.11	2.58	(6) 0.48	1.58	0.03	5.4	(25) 0.84
1.053	0.17	3.92	0.17			2.31	0.08	1.56	0.11	5.0	0.27
1.019	0.17	3.45	(4) 0.67	791. Na <sub>2</sub> CO <sub>3</sub>		2.22	0.16	1.52	0.05	4.25	0.33
		2.94	(6) 1.00	3.43	0.08	2.02	0.16			3.93	(30) 1.00
		2.60	0.17	3.22	0.12	1.97	0.08	799. NaClO <sub>4</sub> ·H <sub>2</sub> O		3.78	0.07
		2.27	0.17	2.96	(40) 0.80	1.91	0.08	5.2	(20) 0.40	3.50	0.27
		2.18	0.33	2.85	0.02	1.73	0.08	4.40	(40) 0.08	3.32	0.10
		2.02	0.17	2.70	0.20	1.52	0.08	3.65	(50) 1.00	3.17	0.07
		1.94	0.17	2.60	(30) 0.60			3.44	0.80	3.04	(25) 0.84
		1.79	0.33	2.54	(50) 1.00			3.19	0.08	2.91	0.13
		1.56	0.17	2.36	0.40			2.92	0.02	2.82	0.67
				2.25	0.60			2.76	0.20	2.73	0.23
				2.18	0.04			2.66	0.12	2.59	0.03
				2.11	0.14			2.58	0.02	2.42	0.03
				2.02	0.40			2.44	0.12	2.32	0.07
				1.95	0.04			2.20	0.30	2.23	0.10B
				1.88	0.02			2.05	0.08	2.01	0.07
				1.83	0.25			1.95	0.02	1.96	0.07
				1.79	0.12			1.88	0.02	1.90	0.23
				1.71	0.08			1.82	0.14	1.86	0.13
				1.67	0.12B			1.72	0.16	1.79	0.13
				1.62	0.25B			1.70	0.08	1.72	0.07
				1.57	0.08			1.58	0.02	1.68	0.10
				1.52	0.16			1.52	0.02	1.66	0.13
				1.482	0.06			1.415	0.04		
				1.451	0.04			1.385	0.03		
				1.418	0.08			1.355	0.02		
				1.388	0.04			1.330	0.02		
				1.347	0.04			1.290	0.03		







(Starred patterns were checked with published crystal structure data)

(Started patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	
(Started patterns were checked with published crystal structure data)												
830. Na <sub>2</sub> O <sub>2</sub>		834. Na <sub>3</sub> PO <sub>4</sub>		837. Na <sub>2</sub> HPO <sub>4</sub> .12H <sub>2</sub> O		840. Na <sub>4</sub> P <sub>2</sub> O <sub>6</sub> .10H <sub>2</sub> O		844. NaNH <sub>4</sub> HPO <sub>4</sub> .4H <sub>2</sub> O		847. NaH <sub>2</sub> PO <sub>3</sub> .H <sub>2</sub> O		
9.0	0.02	4.25	(30)	0.48	7.7	0.10				8.6	0.67	
7.8	0.02	3.95		0.13	6.2	0.10	7.7	0.15	10.1	0.45	7.8	0.67
5.6	0.04	3.84		0.20	5.4	(20)	5.3	0.38	6.6	1.00	6.4	0.40
5.0	0.04	3.45		0.06	4.51		4.90	(25)	5.8	0.10	6.0	0.40
3.75	0.02	3.11		0.11	4.35		4.10		4.6	(10)	4.65	0.07
3.43	0.04	2.70	(30)	0.48	4.00	0.40	3.82	(40)	4.23	0.45	4.16	(12.5) 0.83
3.09	0.10	2.55	(62.5)	1.00	3.73	0.20	3.25		3.67	0.30	3.85	(15) 1.00
2.87	0.04	2.43		0.10	3.47	0.30	2.97	(25)	3.45	0.30	3.70	0.13
2.76	0.02	2.25		0.20	3.30	0.05	2.67		3.27	0.40	3.53	0.83
2.55	(50)	1.00		0.06	3.15	0.05	2.45		3.16	0.05	3.37	0.13
2.47	0.02	2.05		0.20	2.94	(17.5) 0.88B	2.40		3.02	0.05	3.29	0.13
2.42	0.04	1.91		0.48	2.83	0.40	2.33		2.89	(20)	3.12	0.67
2.35	(7)	1.81		0.08	2.71	(12.5) 0.63	2.04	0.05	2.67	0.15	3.00	0.40
2.30	0.12	1.72		0.11	2.58	0.05	1.98	0.15	2.48	0.10	2.87	(15) 1.00
2.24	0.04	1.66		0.02	2.46	0.30	1.86	0.03	2.40	0.10	2.75	0.47
2.03	0.10	1.57		0.06	2.40	0.05	1.77	0.15	2.32	0.10	2.64	0.60
1.96	0.02	1.53		0.24	2.33	0.15	1.68	0.05	2.19	0.15	2.57	0.07
1.89	0.02	1.450		0.11	2.25	0.10	1.63	0.13	2.00	0.10	2.51	0.27
1.86	0.04	1.400		0.03	2.18	0.05	1.59	0.15	1.91	0.10	2.42	0.13
1.80	(25)	0.50B		0.06	2.11	0.15	1.475	0.08	1.82	0.10	2.34	0.13
1.71	0.04	1.316		0.06	2.02	0.10	1.370	0.03	1.77	0.10	2.26	0.13
1.65	0.04	1.275		0.05	1.95	0.15	1.335	0.03	1.73	0.05	2.18	0.27
1.56	0.02	1.245		0.03	1.91	0.25	1.160	0.03			2.12	0.33
1.50	0.04	1.207		0.06	1.82	0.20	1.120	0.03			2.02	0.20
1.466	0.12	1.193		0.08	1.70	0.35	1.050	0.03	845. Sodium Calcium Glycerophosphate		1.99	0.07
1.438	0.04	1.157		0.03	1.65	0.10		0.03			1.94	0.27
1.400	0.04								9.9	0.29	1.86	0.07
1.345	0.12								3.98	(7) 1.00	1.84	0.07
1.275	0.08								2.73	(3) 0.43	1.78	0.40
831. p-C <sub>6</sub> H <sub>4</sub> OH.SO <sub>3</sub> Na.-2H <sub>2</sub> O		835. Na <sub>2</sub> HPO <sub>4</sub>		838. NaH <sub>2</sub> PO <sub>4</sub>		841. NaPO <sub>3</sub>						
		4.90		0.04	4.98	0.08	6.7	0.15				
		4.66		0.03	4.07	0.40	5.3	0.10				
		3.99	(30)	0.40	3.94	(25) 1.00	5.0	(12.5) 0.31				
		3.81	(30)	0.40	3.38	0.40	3.82	0.20				
		3.41		0.20	3.18	(25) 1.00	3.50	0.15				
		2.87		0.17	3.06	0.08	3.39	0.18				
11.9	0.34	2.80	(75)	1.00	2.95	0.16	3.29	0.15			848. Na <sub>2</sub> PbO <sub>3</sub> .3H <sub>2</sub> O	
6.1	0.29	2.71		0.40	2.85	0.04	3.09	(25) 0.63			4.80 (4) 1.00	
5.5	0.06	2.64		0.08	2.72	(12.5) 0.50	2.87	(40) 1.00			4.62 (4) 1.00	
5.0	0.40	2.53		0.11	2.58	0.04	2.73	0.15			4.15 0.25	
4.72	(10)	2.44		0.20	2.48	0.08	2.53	0.15			3.00 0.25	
4.23	0.57	2.30		0.13	2.38	0.16	2.42	0.23			2.90 0.25	
3.99	0.11	2.20		0.20	2.29	0.12	2.28	0.10			2.53 (4) 1.00	
3.81	(17.5)	2.12		0.03	2.23	0.16	2.15	0.03			1.85 0.75	
3.62	0.23	2.05		0.08	2.15	0.16	2.00	0.10			1.73 0.25	
3.41	0.06	1.99		0.20	2.08	0.04	1.85	0.25			1.62 0.25	
3.21	0.23	1.92		0.20	1.97	0.12	1.74	0.10			1.420 0.25	
3.06	(17.5)	1.81		0.08	1.88	0.08	1.68	0.03			1.393 0.25	
2.90	0.11	1.75		0.27	1.84	0.16	1.490	0.08			1.260 0.25	
2.67	0.11	1.71		0.20	1.73	0.16	1.470	0.08				
2.52	0.11	1.63		0.13	1.69	0.04	1.430	0.05				
2.40	0.06	1.59		0.27	1.64	0.16	1.400	0.03				
2.31	0.06	1.470		0.03	1.51	0.08	1.370	0.10				
2.23	0.09	1.445		0.13	1.465	0.08	1.280	0.03				
2.09	0.11	1.400		0.08	1.435	0.04	1.190	0.03				
2.02	0.11	1.344		0.07	1.395	0.04	1.100	0.05				
1.96	0.11											
1.91	0.06											
1.85	0.06											
1.79	0.11											
1.74	0.06											
1.66	0.06											
832. Sodium Nitrophenylate		836. Na <sub>2</sub> HPO <sub>4</sub> .2H <sub>2</sub> O		839. NaH <sub>2</sub> PO <sub>4</sub> .H <sub>2</sub> O		842. Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>						
		5.2	(25)	1.00	5.4	(20) 1.00	4.40	(40) 1.00				
		4.61	(25)	1.00	4.40	0.50	3.38	0.25				
		3.95		0.24	4.18	0.05	2.72	(30) 0.75				
		3.63		0.16	3.91	0.10	2.53	0.03				
		3.34	(20)	0.80	3.77	0.15	2.42	0.03				
		3.24		0.60	3.68	0.25	2.33	0.23				
		2.88		0.60	3.50	0.20	2.06	0.10				
6.1	(17.5)	2.73		0.50	3.39	(20) 1.00	2.02	0.05				
4.23	0.17	2.59		0.24	3.15	(17.5) 0.88	1.91	(12.5) 0.31				
3.45	(10)	2.47		0.60	3.05	0.50	1.75	0.10				
3.25	0.17	2.25		0.28	2.86	0.05	1.67	0.03				
3.00	(4)	2.19		0.24	2.73	0.05	1.55	0.23				
2.81	0.06	2.06		0.24	2.65	0.50	1.475	0.13				
2.60	0.06	2.00		0.16	2.55	0.50	1.424	0.15				
2.35	0.06	1.96		0.20	2.48	0.05	1.342	0.08				
2.29	0.11	1.80		0.28	2.42	0.05	1.293	0.05				
1.72	0.06	1.73		0.04	2.35	0.30	1.206	0.05				
1.52	0.06	1.64		0.12	2.25	0.15	1.165	0.03				
833. Sodium Dinitrophenylate		836. Na <sub>2</sub> HPO <sub>4</sub> .2H <sub>2</sub> O		839. NaH <sub>2</sub> PO <sub>4</sub> .H <sub>2</sub> O		842. Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>						
		5.2	(25)	1.00	5.4	(20) 1.00	4.40	(40) 1.00				
		4.61	(25)	1.00	4.40	0.50	3.38	0.25				
		3.95		0.24	4.18	0.05	2.72	(30) 0.75				
		3.63		0.16	3.91	0.10	2.53	0.03				
		3.34	(20)	0.80	3.77	0.15	2.42	0.03				
		3.24		0.60	3.68	0.25	2.33	0.23				
		2.88		0.60	3.50	0.20	2.06	0.10				
6.1	(17.5)	2.73		0.50	3.39	(20) 1.00	2.02	0.05				
4.23	0.17	2.59		0.24	3.15	(17.5) 0.88	1.91	(12.5) 0.31				
3.45	(10)	2.47		0.60	3.05	0.50	1.75	0.10				
3.25	0.17	2.25		0.28	2.86	0.05	1.67	0.03				
3.00	(4)	2.19		0.24	2.73	0.05	1.55	0.23				
2.81	0.06	2.06		0.24	2.65	0.50	1.475	0.13				
2.60	0.06	2.00		0.16	2.55	0.50	1.424	0.15				
2.35	0.06	1.96		0.20	2.48	0.05	1.342	0.08				
2.29	0.11	1.80		0.28	2.42	0.05	1.293	0.05				
1.72	0.06	1.73		0.04	2.35	0.30	1.206	0.05				
1.52	0.06	1.64		0.12	2.25	0.15	1.165	0.03				
833. Sodium Dinitrophenylate		836. Na <sub>2</sub> HPO <sub>4</sub> .2H <sub>2</sub> O		839. NaH <sub>2</sub> PO <sub>4</sub> .H <sub>2</sub> O		842. Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>						
		5.2	(25)	1.00	5.4	(20) 1.00	4.40	(40) 1.00				
		4.61	(25)	1.00	4.40	0.50	3.38	0.25				
		3.95		0.24	4.18	0.05	2.72	(30) 0.75				
		3.63		0.16	3.91	0.10	2.53	0.03				
		3.34	(20)	0.80	3.77	0.15	2.42	0.03				
		3.24		0.60	3.68	0.25	2.33	0.23				
		2.88		0.60	3.50	0.20	2.06	0.10				
6.1	(17.5)	2.73		0.50	3.39	(20) 1.00	2.02	0.05				
4.23	0.17	2.59		0.24	3.15	(17.5) 0.88	1.91	(12.5) 0.31				
3.45	(10)	2.47		0.60	3.05	0.50	1.75	0.10				
3.25	0.17	2.25		0.28	2.86	0.05	1.67	0.03				
3.00	(4)	2.19		0.24	2.73	0.05	1.55	0.23				
2.81	0.06	2.06		0.24	2.65	0.50	1.475	0.13				
2.60	0.06	2.00		0.16	2.55	0.50	1.424	0.15				
2.35	0.06	1.96		0.20	2.48	0.05	1.342	0.08				
2.29	0.11	1.80		0.28	2.42	0.05	1.293	0.05				
1.72	0.06	1.73		0.04	2.35	0.30	1.206	0.05				
1.52	0.06	1.64		0.12	2.25	0.15						



(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i>	<i>I</i> / <i>I</i> <sub>1</sub>
852. Na <sub>2</sub> SiO <sub>3</sub>		855. Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O		859. Na <sub>2</sub> SO <sub>4</sub> (heated)		862. NaHSO <sub>4</sub> ·H <sub>2</sub> O		866. Na <sub>2</sub> SO <sub>3</sub> ·7H <sub>2</sub> O	
5.3	0.20	5.4	0.16	4.75	0.02	5.2	0.60	8.9	0.05
3.56	0.20	4.75	(40)	4.22	0.01	4.37	0.04	7.9	0.05
3.04	(62.5)	4.17		3.92	(30)	4.00	0.08	7.3	0.05
2.57	(30)	2.96		3.76		3.92	0.08	6.2	0.20
2.40	(40)	2.72		3.51		3.55	(25)	5.7	0.10
1.98	0.09	2.60		2.80	(100)	3.43	(25)	4.95	0.05
1.88	0.28	2.51	(50)	2.63	(50)	2.76		4.70	0.10
1.83	0.09	2.43		2.37		2.64		4.26	0.30
1.75	0.40	2.36		2.24		2.55	(6)	4.00	0.20
1.53	0.05	2.29		2.13		2.42		3.80	0.05
1.445	0.09	2.19		2.08		2.20		3.50	0.10
1.418	0.40	2.10		1.96		2.17		3.31	0.05
1.145	0.03	2.00		1.88		2.10		3.13	0.15
1.114	0.09	1.93		1.74		2.05		3.04	0.10
1.032	0.02	1.85	(20)	1.69		2.00		2.87	1.00
0.990	0.02	1.78		1.61		1.88	(10)	2.66	0.50
0.932	0.02	1.72		1.57		1.82		2.47	0.20
		1.65		1.53		1.78		2.39	0.10
		1.61		1.490		1.73		2.28	0.10
853. Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O		1.53		1.455		1.69		2.17	0.15
8.7	0.10	1.482		1.397		1.62		2.07	0.30
5.9	0.10	1.420		1.380		1.59		2.02	0.05
5.3	0.05	1.390		1.335		1.56		1.94	0.08
5.0	0.10	1.310		1.319		1.51		1.90	0.08
4.75	0.15	1.259		1.298		1.475		1.82	0.10
3.83	(6)	1.161		1.233		1.450		1.72	0.10
3.16		1.143		1.172		1.418		1.56	0.05
2.92	(4)	1.125		1.130		1.382		1.52	0.05
2.79	(20)	1.095		1.090		1.350		1.464	0.05
2.68		1.079		1.052		1.295		1.450	0.05
2.53		1.058		1.010					
2.33		1.035				863. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>		867. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	
2.19		1.014				(50)	0.80	(20)	0.16
2.12		0.993		860. Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O			5.6		4.28
2.02		0.973		6.3	0.03	4.56	0.03		4.39
1.92				5.5	1.00	4.23	0.02		4.15
1.82		856. Na(C <sub>17</sub> H <sub>35</sub> COO)		4.80	0.42	3.90	0.13		3.82
1.71		4.59	(2)	4.33	0.13	3.55	0.02		3.57
1.61		4.16	(10)	3.82	0.27	3.32	0.13		3.03
1.54		3.90	(2)	3.60	0.07	3.19	0.80		2.86
1.51		3.73		3.40	0.07	2.89	0.10		2.82
1.450		3.53		3.22	(15)	2.80	0.05		2.71
1.428				3.10	(15)	2.71			2.60
1.418				2.93		2.63	0.14		2.48
1.399				2.80		2.37	0.02		2.41
1.351				2.70		2.27	0.32		2.28
		857. (CH <sub>2</sub> COONa) <sub>2</sub> ·6H <sub>2</sub> O		2.66	0.10	2.20	0.02		2.24
		5.1	0.48	2.52	0.07	2.08	0.06		2.18
854. NaAlSi <sub>3</sub> O <sub>8</sub>		4.39	0.64	2.44	0.27	1.97	0.10		2.11
6.4	0.08	3.90	(8)	2.37	0.10	1.87	0.05		2.08
4.05	(17.5)	3.58		2.29	0.07	1.78	0.11		2.05
3.80		3.22		2.19	0.07	1.72	0.10		2.02
3.66	(12.5)	3.05		2.10	0.20	1.66	0.06		2.02
3.20	(50)	2.79	(12.5)	2.03	0.07	1.58	0.05		2.02
2.96		2.68		1.97	0.07	1.51	0.03		2.02
2.65		2.55		1.92	0.07	1.455	0.03		2.02
2.56		2.48		1.83	0.17	1.433	0.02		2.02
2.44		2.40		1.79	0.03	1.407	0.02		2.02
2.32		2.17		1.74	0.10	1.377	0.02		2.02
2.18		2.09		1.71	0.07	1.328	0.02		2.02
2.13		2.03		1.66	0.07	1.304	0.02		2.02
1.99		1.96		1.55	0.10	1.278	0.05		2.02
1.90		1.88		1.460	0.03	1.254	0.02		2.02
1.83		1.81		1.370	0.03	1.238	0.03		2.02
1.80		1.72		1.311	0.07	1.186	0.02		2.02
1.73		1.39		1.262	0.07	1.164	0.02		2.02
1.67					0.03	1.131	0.02		2.02
1.58						1.103	0.05		2.02
1.50									2.02
1.460									2.02
1.425									2.02
1.380									2.02
1.350									2.02
1.270									2.02
1.223									2.02
1.200									2.02
1.169									2.02
1.137									2.02
1.050									2.02
1.005									2.02
0.958									2.02
0.910									2.02
0.895									2.02
0.877									2.02
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(Starred patterns were checked with published crystal structure data)

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(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data)

<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>
898. SrHPO <sub>4</sub>		902. S		906. Te*		909. 4TeO <sub>2</sub> ·N <sub>2</sub> O <sub>6</sub> ·1½H <sub>2</sub> O		911. H <sub>2</sub> TeO <sub>4</sub>		915. Tl(NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O					
3.66	(8)	1.00	5.8	0.31	5.8	0.19		8.5	0.03	4.40	(25)	0.63			
3.25	(2)	0.25	3.85	(40)	1.00	3.86	0.14	7.6	7.3	0.03	4.00		0.25		
3.02		0.13	3.45		0.31	3.24	(62.5)	1.00	0.02	4.75		3.11		0.15	
2.87	(4)	0.50	3.21	(20)	0.50	2.34	(30)	0.48	0.06	4.19	(125)	1.00	3.11		0.15
2.60		0.25	3.10	(15)	0.38	2.22	(20)	0.32	0.06	3.19	(100)	0.80	2.95	(40)	1.00
2.44		0.13	2.85		0.38	2.08		0.14	0.06	3.09		0.05	2.44	(17.5)	0.44
2.25		0.25	2.63		0.20	1.96		0.14	0.06	2.71		0.16	2.19		0.20
2.02		0.25	2.50		0.18	1.83		0.28	0.06	2.63	(50)	0.05	1.99		0.10
1.92		0.13	2.43		0.20	1.77		0.10	0.06	2.58		0.40	1.93		0.18
1.84		0.25	2.38		0.15	1.61		0.20	0.05	2.38		0.03	1.75		0.18
1.76		0.13	2.30		0.15	1.470		0.28	0.02	2.30		0.02	1.68		0.18
1.52		0.13	2.12		0.25	1.418		0.13	0.05	2.23		0.03	1.59		0.03
1.430		0.13	2.00		0.03	1.380		0.16	0.80	2.09		0.16	1.55		0.03
1.320		0.13	1.90		0.25	1.309		0.08	0.03	2.03		0.10	1.53		0.03
1.260		0.13	1.83		0.18	1.258		0.05	1.00	1.94		0.10	1.472		0.13
			1.78		0.20	1.175		0.14	0.03	1.88		0.40	1.427		0.05
			1.73		0.18	1.119		0.05	0.02	1.81		0.04	1.398		0.10
			1.66		0.10	1.045		0.05	0.02	1.77		0.16	1.375		0.08
			1.61		0.20	1.005		0.05	0.32	1.73		0.06	1.305		0.03
			1.54		0.03	0.968		0.02	0.06	1.67		0.06	1.270		0.05
			1.480		0.03	0.866		0.02	0.08	1.65		0.06	1.250		0.03
9.7	(15)	1.00	1.480		0.10			2.07	0.03	1.59		0.05	1.222		0.05
6.1		0.13	1.440		0.10			2.00	0.02	1.53		0.08	1.176		0.05
5.1	(6)	0.40	1.425		0.15			1.87	(50)	0.80		0.08	1.150		0.04
4.20		0.27	1.360		0.13			1.72		0.02		0.12	1.134		0.04
3.64	(10)	0.67	1.310		0.03			1.70		0.03		0.06	1.099		0.05
3.38		0.07	1.235		0.03			1.66		0.32		0.03			
3.13		0.13				8.8	0.13	1.59		0.02		0.05			
3.03		0.20				7.7	0.13	1.52		0.13		0.05			
2.55		0.07				6.3	0.25	1.485		0.24		0.05			
2.39		0.07				5.7	0.13	1.443		0.02		0.03			
2.28		0.07	2.33	(20)	1.00	4.54	0.19	1.430		0.02		0.08			
2.13		0.07	1.65	(4)	0.20	4.29	(3)	1.410		0.02					
2.08		0.07	1.346	(6)	0.30	3.90		1.387		0.02					
2.03		0.07	1.165		0.05	3.24	(8)	1.356		0.03					
1.93		0.07	1.042		0.05	3.11		1.308		0.02					
1.83		0.13	0.881		0.05	2.92	(8)	1.292		0.02					
						2.69		1.267		0.20					
						2.60		1.259		0.10					
						2.53		1.227		0.14					
						2.35		1.188		0.02					
						2.23		1.153		0.02					
						2.15		1.133		0.05					
						2.08		1.119		0.10					
						2.00		1.093		0.02					
						1.97		1.075							
						1.91									
						1.87									
						1.83									
						1.77									
						1.71									
						1.66									
						1.64									
						1.61									
						1.58									
						1.56									
						1.54									
						1.480									
						1.460									
						1.423									
						1.377									
						1.312									
						1.261									
						1.204									
						1.181									
						1.120									
						1.087									



TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

(Starred patterns were checked with published crystal structure data/

<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>d</i>	<i>I/I</i> <sub>1</sub>
919. Thorium Acetate		922. Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>		927. SnCl <sub>4</sub> ·5H <sub>2</sub> O		930. SnI <sub>4</sub> *		934. Sn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>		938. SnS*			
9.7	0.24	7.9	(15) 0.75	6.2	(62.5) 1.00	6.9	0.10	6.9	0.07	4.04		0.16	
8.7	(20) 0.80	6.5	(20) 1.00	5.3	(30) 0.48	5.0	0.27	6.1	0.03	3.42	(25)	0.40	
7.5	(25) 1.00	5.0	(15) 0.75	5.0	0.20		0.10	4.39	0.33	3.24	(25)	0.40	
4.71	0.16	4.60	0.05	4.21	0.08	(30)	1.00	3.98	(30) 1.00	2.93	(62.5)	0.32	
4.31	0.08	3.95	0.50	3.86	0.20		0.03	3.42	0.20	2.83		1.00	
4.17	0.08	3.21	0.05	3.70	0.06		0.23	3.11	(30) 1.00	2.30		0.32	
3.76	(8) 0.32	2.98	0.50	3.49	0.05		0.03	2.78	0.20	2.12		0.11	
3.60	0.16	2.88	0.20	3.22	0.11		0.03	2.68	0.27	2.02		0.24	
3.48	0.20	2.70	0.15	3.10	0.06	(15)	0.03	2.48	0.27	1.99		0.24	
3.18	0.20	2.28	0.25	2.94	(17.5) 0.28	(10)	0.50	2.39	0.17	1.87		0.32	
2.90	0.24	2.15	0.15	2.76	0.16		0.33	2.30	0.20	1.78		0.16	
2.78	0.08	2.08	0.05	2.64	0.24		0.03	2.06	0.03	1.72		0.16	
2.63	0.28	2.03	0.10	2.52	0.16		0.03	2.01	0.13	1.69		0.16	
2.48	0.12	1.98	0.15	2.42	0.05		0.03	1.96	0.17	1.62		0.20	
2.34	0.08	1.96	0.15	2.35	0.10		0.05	1.90	0.17	1.56		0.03	
2.23	0.08	1.82	0.05	2.18	0.08		0.10	1.77	(10) 0.33	1.450		0.20	
2.15	0.04	1.79	0.05	2.16	0.06		0.03	1.71	0.07	1.399		0.13	
2.09	0.04	1.75	0.05	2.03	0.16		0.07	1.65	0.07	1.361		0.13	
2.02	0.08	1.73	0.05	1.97	0.16		0.05	1.482	0.07	1.292		0.10	
1.91	0.08	1.70	0.05	1.91	0.05			1.445	0.03	1.262		0.10	
1.87	0.08	1.65	0.05	1.84	0.10					1.224		0.10	
1.83	0.08	1.61	0.05	1.76	0.03	931. SnC <sub>2</sub> O <sub>4</sub>		935. Sn(SO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O		1.197		0.03	
1.78	0.04	1.52	0.05	1.71	0.06	(50)	1.00						
1.73	0.04	1.430	0.05	1.64	0.06	(17.5)	0.35	(30)	1.00	939. SnC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>			
1.70	0.04	1.414	0.05	1.55	0.08	(25)	0.50	(30)	1.00	6.4		0.20	
1.67	0.04	1.285	0.05	1.487	0.03		0.60	(30)	0.30	5.8		0.03	
1.63	0.04	1.267	0.05	1.434	0.02		0.40		0.27	4.89	(20)	0.50	
1.59	0.04			1.402	0.02		0.06		0.33	4.69		0.50	
1.55	0.04			1.360	0.02		0.30		0.42	4.34		0.50	
1.490	0.04	923. ThO <sub>2</sub> *		1.304	0.02		0.30		0.33	3.97		0.44	
1.428	0.04	3.22 (8)	1.00	1.254	0.02		0.25		0.20	3.59	(40)	0.08	
1.399	0.04	2.80	0.38	1.224	0.02		0.25		0.42	3.24		0.08	
1.355	0.04	1.97 (6)	0.75	1.179	0.02		0.20		0.20	2.95	(30)	0.75	
		1.68 (7)	0.88	1.166	0.02		0.20		0.42	2.75		0.08	
920. ThCl <sub>4</sub>		1.399	0.13	1.135	0.02		0.20		0.83	2.65		0.05	
9.1	0.10	1.280	0.38	1.101	0.02		0.04		0.13	2.48		0.18	
7.8	0.10	1.245	0.25	1.075	0.02		0.16		0.07	2.37		0.10	
7.2	(10) 1.00	1.140	0.38	1.057	0.02		0.30		0.83	2.27		0.10	
6.5	(8) 0.80	1.074	0.38				0.02		0.13	2.17		0.15	
5.8	0.10	0.987	0.13		928. (NH <sub>4</sub> ) <sub>2</sub> SnCl <sub>6</sub> *		0.20		0.17	2.11		0.31	
5.4	0.10	0.943	0.25		(75) 1.00		0.12		0.23	2.04		0.13	
4.44	0.10	0.931	0.25	5.8 (75)	0.67		0.06		0.23	1.99		0.10	
4.12	(4) 0.40			5.0 (50)	0.20		0.06		0.50	1.91		0.08	
3.72	0.40	924. Th(SO <sub>4</sub> ) <sub>2</sub>		3.54	0.53		0.02		0.10	1.85		0.20	
3.39	0.30	6.8	0.07	3.02	0.20		0.02		0.13	1.80		0.23	
2.94	0.20	5.9	0.07	2.89	0.53		0.02		0.13	1.74		0.13	
2.67	0.10	4.77 (30)	1.00	2.50	0.20	(75)	0.02		0.13	1.70		0.05	
2.62	0.20	4.23	0.03	2.30	0.13		0.02		0.13	1.65		0.15	
2.52	0.10	4.23	0.10	2.24	0.53		0.02		0.20	1.55		0.18	
2.38	0.10	3.54	0.27	2.04	0.11		0.12		0.20	1.490		0.10	
2.26	0.10	3.30 (8)	0.20	1.93	0.33		0.12		0.20	1.451		0.13	
2.18	0.10	3.03	0.20	1.77	0.67		0.06		0.20	1.408		0.05	
2.06	0.10	2.86 (10)	0.33	1.69	0.33		0.04		0.20	1.372		0.05	
1.95	0.10	2.74	0.17	1.67	0.27		0.02		0.20	1.340		0.03	
1.89	0.10	2.42	0.17	1.58	0.07		0.02			1.305		0.03	
1.83	0.10	2.36	0.17	1.53	0.08		0.02			1.270		0.03	
1.77	0.10	2.28	0.17	1.449	0.17		0.02						
1.73	0.10	2.14	0.17	1.403	0.17		0.02						
1.67	0.10	2.08	0.27	1.340	0.07		0.02						
1.63	0.10	2.04	0.27	1.307	0.13		0.04						
1.59	0.10	1.88	0.27	1.254	0.07		0.02						
		1.79	0.27	1.217	0.13		0.04						
		1.70	0.20	1.182	0.05		0.02						
		1.65	0.20	1.158	0.09		0.02						
		1.57	0.17	1.121	0.13		0.02						
		1.490	0.13	1.099	0.11		0.02						
		1.440	0.13				0.02						
		1.419	0.13				0.02						
		1.370	0.07				0.02						
		1.309	0.07				0.02						
		1.285	0.07				0.02						
		1.175	0.07				0.02						
		1.163	0.10				0.02						
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TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Continued)

(Starred patterns were checked with published crystal structure data)

d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
943. K <sub>2</sub> TiF <sub>6</sub> ·H <sub>2</sub> O		948. WO <sub>3</sub>		953. Vanadium Chloride		957. Y(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O		961. Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O		966. Zn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	
4.95 (12.5)	0.19	3.81 (30)	1.00	11.4 (40)	1.00	8.4 (10)	1.00	6.8 (10)	0.33	6.9 (50)	1.00
4.65	0.09	3.65 (12.5)	0.42	5.6 (40)	1.00	5.7 (6)	0.60	5.4 (30)	1.00	6.0	0.04
3.39 (40)	0.59	3.34	0.13	5.2	0.05	5.3 (8)	0.80	5.0	0.03	4.79	0.30
2.85	0.26	3.15	0.23	4.30	0.25	4.65	0.20	4.7	0.27	4.45	0.02
2.47	0.08	2.65 (17.5)	0.58	4.00	0.18	4.24	0.20	4.45 (25)	0.83	4.22	0.10
2.34	0.15	2.52	0.03	3.68	0.05	3.91	0.20	4.00	0.20	4.05	0.20
2.18 (67.5)	1.00	2.44	0.10	3.50	0.10	3.23	0.30	3.80	0.33	3.82	0.12
2.10	0.14	2.16	0.23	3.30	0.08	3.04	0.15	3.58	0.27	3.60	0.25
1.73	0.10	2.02	0.07	3.11	0.03	2.98	0.20	3.28	0.27	3.18 (12.5)	0.08
1.69	0.19	1.92	0.07	3.01	0.03	2.92	0.15	3.20	0.27	3.05	0.20
1.65	0.05	1.82	0.27	2.78	0.75	2.79	0.20	3.01	0.03	2.90	0.08
1.460	0.09	1.70	0.13	2.71	0.03	2.61	0.20	2.85	0.13	2.71	0.12
1.430	0.12	1.65	0.27	2.63	0.25	2.53	0.30	2.70	0.17	2.52	0.04
1.362	0.08	1.59	0.03	2.52	0.25	2.39	0.20	2.40	0.17	2.41	0.12
1.318	0.08	1.54	0.07	2.42	0.03	2.30	0.20	2.30	0.03	2.30	0.06
1.196	0.03	1.490	0.13	2.34	0.03	2.22	0.10	2.14	0.07	2.13	0.06
1.135	0.05	1.389	0.03	2.24	0.08	2.12	0.60	2.04	0.07	2.08	0.02
944. TiO <sub>2</sub> * (anatase)		1.309	0.03	2.15	0.08	2.05	0.15	2.00	0.03	2.02	0.08
3.52 (62.5)	1.00	1.240	0.13	2.00	0.10	1.98	0.20	1.96	0.07	1.97	0.04
2.37	0.24	1.179	0.03	1.93	0.05	1.95	0.10	1.80	0.03	1.91	0.04
1.88 (25)	0.40	1.160	0.03	1.82	0.15	1.92	0.20	1.76	0.03	1.87	0.10
1.70 (17.5)	0.28	1.121	0.03	1.67	0.10	1.89	0.10	1.68	0.05	1.80	0.04
1.66	0.24	949. UO <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O		1.63	0.10	1.86	0.10	1.60	0.03	1.74	0.04
1.480	0.24	8.1 (7)	0.78	1.55	0.03	1.83	0.10	1.58	0.03	1.67	0.06
1.362	0.08	6.3 (8)	0.89	1.51	0.08	1.79	0.15	1.50	0.03	1.58	0.04
1.335	0.08	5.9	0.67	1.440	0.03	1.76	0.15	962. ZnAl <sub>2</sub> O <sub>4</sub> *		1.480	0.02
1.262	0.11	5.2	0.45	1.390	0.03	1.70	0.15	2.85 (8)	0.53	1.445	0.02
1.164	0.06	4.59 (9)	1.00	1.330	0.03	1.65	0.10	2.44 (15)	1.00	967. Zinc Chloride (fused)	
1.045	0.03	4.44	0.44	1.260	0.03	1.61	0.10	2.02	0.07	4.79 (20)	0.67
0.950	0.02	3.91	0.44	954. V <sub>2</sub> O <sub>5</sub> *		958. Y <sub>2</sub> O <sub>3</sub> *		1.91	0.07	3.06 (30)	1.00
0.913	0.02	3.72	0.44	3.65 (30)	0.60	4.29	0.02	1.85	0.07B	2.90	0.17
0.894	0.02	3.44	0.56	2.70 (40)	0.80	3.05 (50)	1.00	1.65	0.13	2.34	0.20
945. TiO <sub>2</sub> * (rutile)		3.13	0.17	2.47	0.60	2.64	0.16	1.55	0.33	1.97	0.10
3.24 (40)	0.80	2.95	0.33	2.32	0.02	2.50	0.03	1.480	0.07	1.91	0.10
2.49 (30)	0.60	2.72	0.44	2.18	0.20	2.37	0.02	1.431 (6)	0.40	1.86 (10)	0.33
2.29	0.04	2.52	0.33	2.03	0.02	2.26	0.03	1.232	0.07	1.62	0.10
2.19	0.30	2.41	0.22	1.83 (50)	1.00	2.07	0.04	963. Zn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O		1.57	0.10
2.05	0.12	2.24	0.33	1.61	0.02	1.93	0.02	7.9 (10)	0.80	968. ZnCrO <sub>4</sub>	
1.69 (50)	1.00	2.11	0.11	1.57	0.03	1.87 (20)	0.40	6.2	0.24	9.5 (15)	0.38
1.62	0.30	2.02	0.17	1.470	0.25	1.81	0.02	5.5	0.32	4.67	0.38
1.485	0.20	1.97	0.11	1.429	0.30	1.71	0.02	4.90	0.24	3.10	0.23
1.449	0.20	1.90	0.11	1.330	0.10	1.64	0.02	4.60	0.72	2.67	1.00
1.355	0.30	1.80	0.22	1.235	0.04	1.60 (15)	0.30	4.25	0.12	2.53	0.03
1.245	0.04	1.74	0.11	1.218	0.02	1.56	0.02	3.60	0.16	2.44	0.15
1.170	0.08	1.64	0.11	1.193	0.02	1.52	0.02	3.25 (12.5)	1.00	2.34	0.03
1.147	0.04	1.60	0.11	1.170	0.06	1.343	0.02	2.98	0.48	2.24	0.13
1.091	0.08	1.53	0.11	1.125	0.03	1.322	0.04	2.79 (10)	0.80	2.14 (17.5)	0.43
1.040	0.08	1.483	0.11	1.093	0.06	1.215	0.03	2.70	0.40	1.95	0.05
0.964	0.04	1.445	0.11	1.057	0.06	1.186	0.02	2.62	0.32	1.85	0.05
0.903	0.02	1.310	0.11	955. V <sub>2</sub> O <sub>5</sub> *		1.141	0.02	2.53	0.08	1.75	0.03
0.890	0.08	950. UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O*		5.7	0.33	1.116	0.02	2.45	0.32	1.60	0.13
0.875	0.04	6.6 (10)	0.80	4.38 (15)	1.00	959. Zn*		2.16	0.48	1.57	0.25
0.843	0.02	5.7 (12.5)	1.00	4.09	0.13	2.46 (12.5)	0.25	2.05	0.08	1.480	0.03
0.832	0.04	4.33 (12.5)	1.00	3.39 (12.5)	0.83	2.30 (10)	0.20	1.98	0.16	1.466	0.20
0.822	0.04	3.63	0.08	2.87 (8)	0.53	2.08 (50)	1.00	1.83	0.40	1.398	0.05
946. W*		3.29	0.56	2.76	0.13	1.68	0.14	1.67	0.08	1.350	0.05
2.23 (17.5)	1.00	2.93	0.08	2.61	0.13	1.330	0.18	1.62	0.40	1.294	0.03
1.58	0.29	2.85	0.08	2.18	0.07	1.169	0.12	1.58	0.16	1.265	0.03
1.290 (12.5)	0.71	2.62	0.16	1.99	0.07	1.120	0.08	1.51	0.24	1.195	0.03
1.117	0.17	2.54	0.12	1.92	0.13	1.040	0.02	1.485	0.32	1.145	0.03
1.000	0.29	2.46	0.24	1.86	0.07	0.941	0.02	1.400	0.08	1.123	0.03
0.913	0.06	2.37	0.12	1.77	0.10	0.905	0.02	960. Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>		1.100	0.05
0.846	0.34	2.28	0.24	1.65	0.07	964. Zinc Arsenite		4.00 (8)	0.53	1.070	0.03
0.745	0.11	2.17	0.16	1.56	0.07	7.5 (50)	1.00	3.40 (15)	1.00	1.020	0.03
0.707	0.06	2.11	0.16	1.51	0.07	4.55 (30)	0.60	3.15 (5)	0.33	969. Zn(CN) <sub>2</sub>	
0.674	0.06	1.98	0.08	1.490	0.07	4.22	0.12	2.95	0.33	4.19 (75)	1.00
0.622	0.06	1.89	0.48	1.452	0.07	4.02	0.12	2.63	0.13	3.40	0.13
947. H <sub>2</sub> W <sub>4</sub> O <sub>13</sub>		1.84	0.08	1.305	0.07	3.68 (17.5)	0.35	2.40	0.13	2.95	0.04
5.3 (20)	0.50	1.71	0.12	956. (VO) <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·16H <sub>2</sub> O		3.46	0.10	2.18	0.13	2.40	0.40
3.48 (40)	1.00	1.64	0.12	6.3	0.32	3.28	0.08	2.01	0.07	2.08 (20)	0.27
2.93	0.08	1.54	0.12	5.8	0.32	3.12	0.08	1.95	0.07	1.86	0.11
2.69	0.05	951. V*		5.4	0.32	2.90	0.02	1.83	0.07	1.70	0.01
2.60	0.10	2.14 (100)	1.00	5.1	0.08	2.80	0.02	1.68	0.13	1.57	0.20
2.55 (10)	0.25	1.51 (7)	0.07	4.55 (25)	1.00	2.72	0.04	1.55	0.13	1.470	0.01
2.37	0.10	1.236 (20)	0.20	4.35 (12.5)	0.50	2.60	0.02	1.435	0.20	1.390	0.07
2.31	0.08	1.072	0.03	3.90	0.24	2.39	0.04	1.380	0.07	1.315	0.03
2.23	0.03	0.958	0.03	3.70	0.16	2.29	0.10	965. Zn(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub>		1.256	0.01
2.10	0.03	0.875	0.01	3.51 (12.5)	0.50	2.20	0.10	11.0 (12.5)	1.00	1.202	0.01
1.97	0.08	0.810	0.03	3.30	0.28	2.12	0.04	9.8 (6)	0.48	1.157	0.03
1.84	0.20	0.759	0.01	3.16	0.16	2.06	0.08	8.4	0.16	970. Zinc Potassium Cyanide	
1.73	0.15	0.714	0.01	3.04	0.28	2.01	0.04	7.5	0.48	4.44 (15)	0.37
1.69	0.03	952. VC*		2.82	0.28	1.97	0.02	5.3	0.32	3.79 (40)	1.00
1.63	0.13	2.40 (40)	1.00	2.70	0.24	1.90	0.02	4.90	0.40	3.14	0.10
1.60	0.08	2.07 (40)	1.00	2.64	0.28	1.79	0.04	4.51	0.24	2.57	0.05
1.50	0.05	1.469 (20)	0.50	2.47	0.12	1.72	0.04	4.27	0.64	2.42	0.15
1.470	0.05	1.251	0.25	2.34	0.20	1.67	0.02	4.10	0.16	2.22 (10)	0.25
1.410	0.03	1.199	0.10	2.18	0.20	1.62	0.06	3.92	0.08	1.98	0.02
1.305	0.03	1.039	0.05	2.03	0.08	1.56	0.04	3.55	0.16	1.92	0.05
1.276	0.03	0.952	0.05	1.98	0.08	1.485	0.02	3.33	0.12	1.68	0.05
1.245	0.03	0.929	0.10	1.88	0.04	1.440	0.02	3.13	0.08	1.63	0.05
1.215	0.03	0.849	0.05	1.75	0.04	1.405	0.02	3.05	0.08	1.480	0.02
1.189	0.03	0.800	0.03	1.64	0.04	1.374	0.02	2.90	0.08	1.458	0.02
1.157	0.05			1.55	0.04			2.71	0.08		
				1.450	0.03			2.61	0.08		
								2.46	0.08		
								2.23	0.03		



(Starred patterns were checked with published crystal structure data)

(Started patterns were checked with published crystal structure data)

$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$	$d$	$I/I_1$								
(Started patterns were checked with published crystal structure data)																	
971. $\text{Zn}_2\text{Fe}(\text{CN})_{10}\cdot 3\text{H}_2\text{O}$			976. $\text{ZnC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$			981. $\text{Zn}(\text{C}_6\text{H}_5\text{OHSO}_3)_2\cdot 8\text{H}_2\text{O}$			984. $\text{ZnHPO}_3\cdot 2\frac{1}{2}\text{H}_2\text{O}$			987. $\text{ZnSO}_4\cdot \text{H}_2\text{O}$			990. $\text{ZnSO}_4\cdot \text{K}_2\text{SO}_4\cdot 6\text{H}_2\text{O}$		
5.4	(17.5)	0.88	4.73	(75)	1.00	13.7	0.50	7.7	0.20	4.80	(40)	0.64	7.1		0.03		
4.51		0.35	3.93	(12.5)	0.17	12.3	0.10	6.3	0.13	3.80		0.11	6.2		0.20		
4.08	(20)	1.00	3.58	25)	0.33	5.7	0.30	5.9	0.13	3.40	(62.5)	1.00	5.4		0.10		
3.64	(8)	0.40	2.66		0.13	5.3	0.20	5.3	0.20	3.06	(25)	0.40	5.2		0.07		
3.11		0.30	2.55		0.11	5.1	0.20	4.38	(10)	0.25		0.40	4.4		0.13		
3.00		0.05	2.23		0.11	4.80	(20)	3.77	(40)	1.00		0.06	4.14	(30)	1.00		
2.70		0.20	2.15		0.03	4.66	(20)	3.60	(25)	0.63		0.11	3.68	(30)	1.00		
2.54		0.20	2.08		0.05	4.31		3.39		0.13		0.14	3.31		0.20		
2.37		0.10	2.03		0.04	3.98	(15)	3.11		0.10		0.10	3.15		0.03		
2.32		0.05	1.99		0.01	3.54		3.01		0.25		0.13	3.06		0.27		
2.20		0.10	1.92		0.07	3.35		2.88		0.13		0.08	2.97		0.33		
2.08		0.05	1.88		0.07	3.35		2.80		0.20		0.08	2.82		0.27		
2.03		0.05	1.80		0.05	3.15		2.70		0.10		0.03	2.74		0.03		
1.95		0.05	1.76		0.05	3.05		2.54		0.10		0.11	2.65		0.03		
1.89		0.05	1.69		0.01	2.85		2.43		0.25		0.08	2.51		0.10		
1.80		0.05	1.65		0.01	2.70		2.20		0.15		0.08	2.37	15)	0.50		
1.69		0.05	1.59		0.01	2.58		2.15		0.18		0.02	2.25		0.03		
1.56		0.05	1.55		0.01	2.46		2.07		0.10		0.05	2.20		0.27		
1.480		0.05	1.52		0.01	2.31		1.98		0.05		0.05	2.13		0.07		
			1.480		0.01	2.23		1.90		0.15		0.02	2.06		0.20		
			1.427		0.01	2.06		1.86		0.03		0.02	1.99		0.07		
			1.367		0.01	1.98		1.81		0.13		0.02	1.93		0.03		
			1.245		0.01	1.91		1.75		0.05		0.03	1.87		0.07		
						1.84		1.72		0.03		0.03	1.83		0.07		
						1.81		1.68		0.05			1.77		0.07		
						1.77							1.73		0.07		
						1.69							1.68		0.07		
						1.450							1.62		0.03		
													1.57		0.03		
													1.51		0.03		
													1.460		0.03		
													1.432		0.03		
													1.400		0.03		
													1.360		0.03		
													1.321		0.03		
													1.300		0.03		
													1.282		0.03		
													1.260		0.03		
													1.206		0.03		
													1.191		0.03		
													1.142		0.03		
													1.121		0.03		



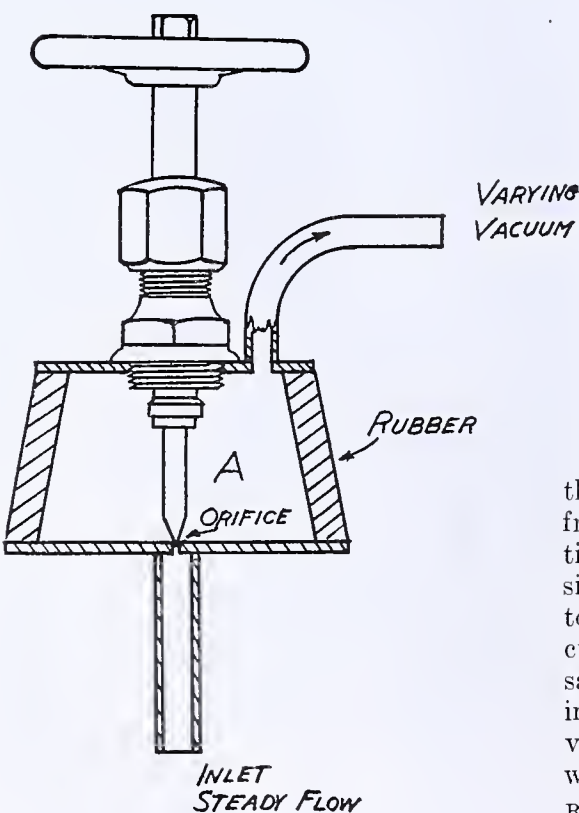
TABLE XII. POWDER DIFFRACTION DATA FOR 1000 CHEMICAL SUBSTANCES (Concluded)

(Starred patterns were checked with published crystal structure data)									
d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
994. (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> COO) <sub>2</sub> Zn.2H <sub>2</sub> O		995. Zr*		997. Zr(NO <sub>3</sub> ) <sub>4</sub> .5H <sub>2</sub> O		998. ZrO <sub>2</sub> * (Monoclinic)		999. ZrSiO <sub>4</sub> *	
12.5	(62.5) 1.00	2.78	(12.5) 0.31	9.6	(40) 1.00	5.1	0.05	4.43	0.50
7.2	0.03	2.56	(8) 0.20	6.9	(40) 1.00	3.29	0.24	3.29	1.00
6.3	0.06	2.44	(40) 1.00	6.1	0.05	3.69	1.00	2.64	0.04
5.5	0.10	1.88	0.18	5.2	0.10	3.19	(125) 1.00	2.51	(100) 1.00
4.85	(30) 0.48	1.61	0.18	4.73	(20) 0.50	2.85	(100) 0.80	2.33	0.13
4.55	(15) 0.24	1.460	0.18	4.21	0.18	2.63	0.32	2.21	0.15
4.25	0.08	1.360	0.15	3.64	0.20	2.55	0.16	2.05	0.30
3.78	0.24	1.343	0.10	3.49	0.15	2.34	0.08	1.90	0.25
3.57	0.10	1.282	0.05	3.25	0.38	2.21	0.24	1.74	0.15
3.10	0.08	1.220	0.03B	3.03	0.10	2.01	0.16	1.71	(75) 0.75
2.98	0.03	1.180	0.03B	2.56	0.18	1.85	0.32	1.64	0.25
2.87	0.02	1.082	0.05	2.43	0.15	1.81	(50) 0.40	1.54	0.03
2.70	0.06	1.038	0.08	2.33	0.15	1.70	0.20	1.479	0.15
2.57	0.05	1.003	0.03	2.17	0.15	1.66	0.24	1.380	0.20
2.48	0.02	0.977	0.03	2.13	0.15	1.62	0.05	1.360	0.15
2.35	0.06	0.898	0.03	2.07	0.13	1.59	0.06	1.285	0.06
2.30	0.03	0.877	0.03	1.98	0.13	1.55	0.24	1.255	0.20
2.24	0.02			1.91	0.08	1.51	0.08	1.210	0.02
2.19	0.03	996. ZrOCl <sub>2</sub> .8H <sub>2</sub> O		1.81	0.10	1.486	0.16	1.185	0.18
2.12	0.03	12.8	(15) 1.00	1.74	0.08	1.426	0.16	1.163	0.03
2.07	0.06	10.6	0.27	1.70	0.05	1.363	0.05	1.098	0.15
2.02	0.05	7.9	0.20	1.64	0.10	1.330	0.08	1.057	0.08
1.96	0.05	6.9	(10) 0.67	1.59	0.03	1.307	0.03	1.046	0.13
1.88	0.06	4.80	0.13	1.55	0.05	1.270	0.12	0.999	0.04
1.81	0.03	4.12	0.27	1.51	0.03	1.219	0.05	0.972	0.10
1.76	0.03	3.82	0.20	1.476	0.03	1.167	0.06		1.090
1.69	0.05	3.60	(12.5) 0.83	1.390	0.03	1.113	0.06		1.053
1.60	0.03	3.24	0.40	1.360	0.05	1.036	0.04		
1.490	0.03	2.96	0.07	1.295	0.03	1.001	0.06		
		2.74	0.07	1.228	0.03				
		2.55	0.07						
		2.39	0.07						
		2.22	0.13						
		2.15	0.20						
		2.07	0.13						
		2.00	0.07						
		1.91	0.13						
		1.81	0.13						
		1.71	0.13						
		1.62	0.13						
		1.57	0.07						
		1.51	0.07						
		1.460	0.07						
		1.423	0.07						

A Compact Self-Regulating Valve

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IN CONNECTION with collecting air samples by means of an evacuated chamber, a constant rate of flow of the sample was required as the vacuum in the chamber dropped. The controlling device had to be compact, light, and sufficiently strong to stand a lot of abuse. The volume of the chamber was approximately 1 cubic foot, and it was desired to sample this volume in about 3 minutes.

The valve as illustrated was made from materials at hand and performed well. A No. 10 rubber stopper was cut out to leave a 0.19-inch wall and two 0.063-inch brass plates were vulcanized over the open ends. In the center of one plate was drilled a 0.047-inch orifice and a copper connecting tube was soldered on. In the center of the other plate was soldered a 0.125-inch valve stem and packing gland. The original valve needle had been cut away and a smaller long needle set in its place. This end plate also contained the 0.25-inch vacuum connection.

As the vacuum in chamber A varies, the end plates move accordingly and the orifice adjusts the flow to an approximately constant value. There is no friction involved in the movement and the adjustment takes place without any time lag. With the full vacuum applied, the needle was screwed in until the desired rate of flow was attained, and it was found that the flow remained constant to within 10 per cent for a variation of vacuum from 28 down to 2 inches of mercury, below which the flow fell off at a rate depending on the friction in the sampling system. The steadiness of flow may be improved by suitably shaping the point of the needle valve. By a reverse arrangement of the needle, the valve may be adapted for governing air flow from a pressure source. The valve worked surprisingly well and can be refined and adapted to other purposes.

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# Determining Dissolved Water in Liquefied Gases

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THE production and use of the many liquefied gases commercially available today frequently bring up the problem of contamination by small amounts of dissolved water. Instances of trouble from this impurity are the freezing of pressure regulators in the domestic use of liquefied petroleum gases, the freezing of controls in solid carbon dioxide manufacture, and the attendant corrosion with liquefied hydrogen sulfide. In order to eliminate these difficulties it is necessary to have an accurate analytical procedure for studying the behavior of this impurity during production and use. In some cases a study of this sort may reveal methods of dehydrating, such as fractionation of an azeotrope of water-liquid gas, to replace more expensive and less effective methods (2).

The source of sample *A* is shown inverted in Figure 1, so that liquefied gas is led up to the point of vaporization, valve *C*, where the function of the steam jet, *B*, is to prevent dehydration due to the expansion cooling effect. This jet also has the function of vaporizing any liquid that goes beyond valve *C*, thus preventing pressure surges.

By proper manipulation of needle valves *C* and *E*, the pressure of the gas to be tested can be adjusted so that no sudden surges occur.

If connections and apparatus of ordinary size are used, a positive reading of 0.25 to 1 inch of mercury will suffice to overcome the pressure drop through the remainder of the testing train. The connections between the different parts of the apparatus are 0.125-inch copper or glass tubing, as far as possible, with a minimum of rubber for flexibility, if the gas being tested does not attack this substance.

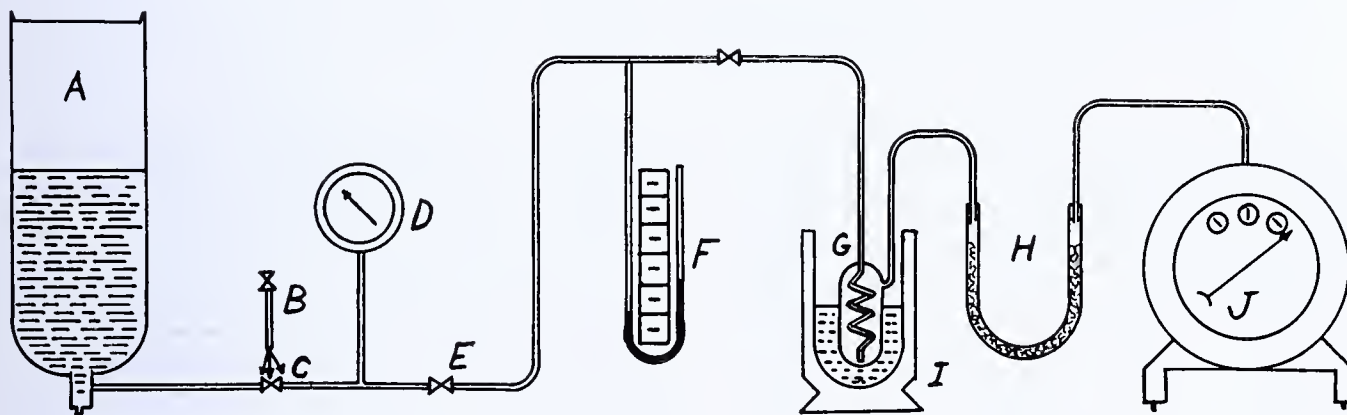


FIGURE 1. DIAGRAM OF EQUIPMENT

The method described below has been developed for the analysis of dissolved water, is accurate to within  $\pm 0.005$  per cent water content, and may be used down to 0.005 per cent, although below 0.01 per cent the accuracy is not very great. Its manipulation is easily learned, and the apparatus is ordinarily available in any laboratory except for the glass freezing bulb and the necessary liquid air or similar refrigerating gas. Any gas with a boiling point a few degrees lower than the one being tested may be used, if the same pressure is used for both the tested and cooling gases.

Analyses are made by freezing the water out of solution by subjecting the vapor to a low-temperature area of condensed gas kept in that state by the cooling medium. The necessary equipment is shown connected for use in Figure 1.

## Equipment

*A* is the source of sample, and *B* is a small jet of steam impinging on the 0.125-inch needle expansion valve, *C*, where most of the expansion to atmospheric pressure takes place. It is necessary to keep only 5 to 13 pounds pressure on the Bourdon gage, *D*, between needle valves *C* and *E*. Valve *E* is the final regulation of gas pressure into the testing apparatus, measured by the mercury U-tube, *F*. Next in line is the freezing bulb, *G*, where the moisture is collected, and which is protected from meter moisture by the phosphorus pentoxide U-tube, *H*. The Pyrex freezing bulb is shown in larger size in Figure 2, and consists simply of a three-turn glass spiral sealed into a chamber of similar material with an exit tube at the top. The bottom of the spiral fits into a small hemispherical depression and comes to within 0.125 inch of the depression bottom. The final piece of apparatus in the train is the usual type of wet-test meter, *J*. *I* is a wide-mouthed thermos container of the refrigerating gas.

## Test Procedure

At the start of a test the entire train is hooked up to the source of sample and gas is allowed to run through the apparatus for several minutes. The freezing bulb must be dry and clean at the beginning. After flushing the bulb out for a few minutes it is removed from the train, held in an upright position (if the gas being tested is heavier than air), and stoppered at both the exit and entrance tubes. The bulb is now weighed carefully on an analytical balance, using a counterbalancing bulb for accuracy. Since the quantity of moisture to be extracted from a reasonable quantity of gas is small, the bulb must be handled very carefully at all times. During this period a short piece of glass tubing should be substituted for the freezing bulb and the gas allowed to course through the testing train at normal pressure and atmospheric temperature. After the weighing is completed the test is ready to begin.

Careful manipulation is necessary during the first part of a test. The gas is shut off temporarily and the meter reading is recorded. Then the gas is turned on slowly and condensed in the freezing bulb as fast as it enters the system, thus keeping the meter hand from moving as far as possible. A slight forward movement of the counter is to be desired rather than a backward one, since the latter indicates a too rapid condensation of gas and consequent danger of contamination by back suction of air or moisture from the exit. The condensation is brought about by raising the thermos container of refrigerating gas around the freezing bulb. It may be found that alternate raising and lowering of the

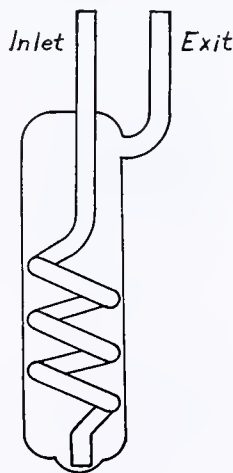


FIGURE 2. PYREX FREEZING BULB



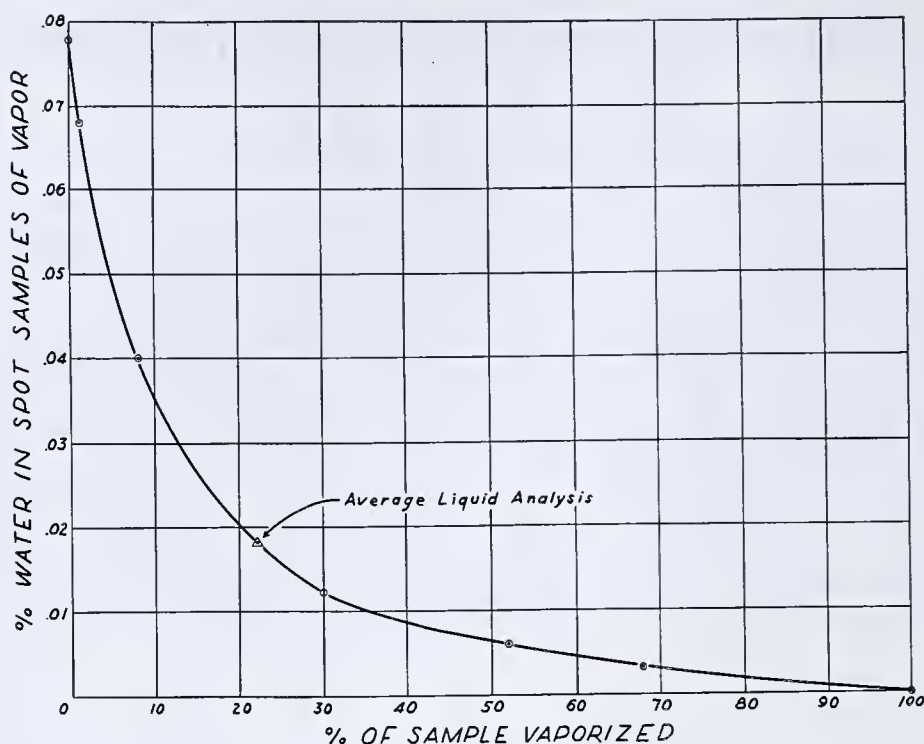


FIGURE 3. AZEOTROPISM OF PROPANE-WATER MIXTURE AT 80° F.

thermos is necessary to prevent too rapid liquefaction. After the liquefied gas fills the Pyrex bulb approximately half full, or covers the spiral, the thermos is adjusted to such a height below the bulb that the liquid level remains constant. Gas will then be condensed as fast as it leaves the system, and the rate of flow should be adjusted to approximately 0.02 to 0.05 cubic foot per minute. For dissolved water contents of from 0.01 to 0.1 per cent by weight, 1 or 2 cubic feet of gas will ordinarily be sufficient for an accurate determination, although within limits the greater the sample tested the better will be the accuracy.

When sufficient gas has passed through the cold area to secure a visible amount of frozen moisture in the spiral, the flow is stopped and the part of the train preceding the bulb is closed off by a pinchcock. The thermos is removed from the outside of the bulb and the condensed gas inside is allowed to boil off to dryness. Enough pressure will be built up spontaneously to run the meter and measure this additional quantity of gas—a necessary procedure, since this is part of the tested material. It will be found that additional moisture in the form of frost is left in the bottom of the outer glass chamber when the last of the tested sample has boiled off. At this point the bulb is removed from the train, sealed with the same stoppers as before, and again weighed, after carefully drying the outside. Just before this second weighing the exit tube stopper should be opened for a moment to relieve any pressure above atmospheric brought about by warming the gas in the bulb to room temperature. It is necessary to perform both weighings with the gas in the bulb at approximately the same temperature and pressure.

The increase in weight is due to the moisture extracted from the volume of gas measured by the meter, if there has been no interference from other factors, such as the condensation of heavy fractions dissolved in the gas.

The type of bulb shown in Figure 2 is sufficiently efficient to freeze out substantially all the moisture in the gas. This has been checked by placing two bulbs in series during a test, where the first bulb duplicated results with a single bulb on the same sample, and the second increased in weight by a negligible amount compared to the first.

To substantiate the statement that accuracy within  $\pm 0.005$  per cent is obtainable, Table I gives check tests on liquefied petroleum gases.

In Figure 1 the sample is shown inverted so that the liquid phase is maintained up to the vaporizing point, valve C. This procedure is necessary if error due to azeotropism is to be avoided. One of the chief values of this testing method is to study the azeotropism of such gas-water mixtures. An average analysis of the liquid is obtained by testing the sample

inverted; then by testing successive fractions with the sample upright a history of the vaporization of a batch of the liquefied gas is obtained. In the case of propane-water mixtures azeotropism is found to exist, as shown by Figure 3, the curve of which was obtained by the above method. Such information is valuable when dehydration on a large scale is necessary.

Some liquefied gases form hydrates, as in the case of propane, which takes on 6 molecules of water to give the solid white compound  $C_3H_8 \cdot 6H_2O$ . The effect of low temperature on this type of compound is not known, but the moisture ordinarily collected is probably free dissolved water, and other means would be necessary for determining molecular water.

It may be desirable to vary the pressure of the gas in the testing train for certain gases. This gives the investigator choice of test temperatures for any given cooling medium. Constructing apparatus for this is usually not worth while however.

TABLE I. CHECK TESTS ON LIQUEFIED PETROLEUM GASES

Sample	Test No.	Weight Per Cent of $H_2O$ in Liquefied Gas
Propane-propylene mixture	1	0.040
	2	0.037
	3	0.040
	4	0.041
100% propane	1	0.020
	2	0.025

This method of water determination may be applied to any gases with boiling points between that of the refrigerating gas and approximately 0° F. Above this temperature errors due to water loss become sufficiently great to prevent an accurate determination. For practical testing the method is recommended as being easily adaptable to routine work and of reasonable accuracy. It has been found superior in accuracy to similar determinations by phosphorus pentoxide absorption, cobalt bromide color indication, and wet- and dry-bulb thermometry, as recommended by other investigators (1, 2).

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# A Drastic Saponification Method for Difficultly Saponifiable Esters

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THE problem of quantitatively saponifying esters that are resistant to alkali has been encountered many times. Kossel and Obermüller (8), Kossel and Krüger (7), Obermüller (10), and Beythien (2) all used sodium ethoxide dissolved in a low-boiling solvent to effect the complete saponification of certain fats and of difficultly saponifiable waxes, such as ceresin. Pardee and Reid (12) and Pardee, Hasche, and Reid (11) used butyl alcohol as a saponification medium and obtained results that were in general a little higher than those obtained when the saponifications were carried out in the presence of ethanol. The reagent used by Steet (15) for his saponification work consisted of a solution of potassium hydroxide in ethylene glycol monoethyl ether. As a saponification reagent for twelve common esters, Redemann and Lucas (13) used a solution of potassium hydroxide in diethylene glycol. They obtained theoretical results by heating their reaction mixtures at 120° to 130° C. for only 3 minutes. Kesler, Lowy, and Faragher (3, 4) saponified ethyl abietate by heating it with alcoholic potassium hydroxide at 40° to 150° C. in a sealed glass tube, getting a saponification value of 170.1 instead of the theoretical 169.8. (Throughout this paper the term "saponification value" is used to denote the number of milligrams of potassium hydroxide required to saponify 1 gram of sample.) Allen, Meharg, and Schmidt (1) saponified certain resins by heating them in an autoclave for several hours with 10 or 15 per cent sodium hydroxide, presumably not attempting to get quantitative results. Smith (14) has discussed comprehensively the effect of the use of various solvents in saponification.

The writers wished to have available a quantitative method suitable for saponifying such terpene esters as bornyl and phenyl phthalates as well as esters of abietic acid. One difficulty involved in accomplishing this consists in finding a solvent with a sufficiently high boiling point which does not get discolored by strong alkali, as do most primary alcohols other than methanol. A reagent obtained by dissolving sodium in tertiary butyl alcohol, used in glass apparatus and in accordance with the usual procedure, proved entirely satisfactory for the saponification of bornyl phthalate. In two experiments the results on carefully purified dibornyl phthalate were 254.7 and 254.7, respectively, instead of the theoretical value of 255.9. When the usual saponification procedure was applied to this specimen, a saponification value of only 57 was obtained. Abietic acid esters are extremely resistant to alkali. Ethyl abietate has a theoretical saponification value of 169.8. When it was treated for 1 hour merely with alcoholic potassium hydroxide, the usual procedure, a saponification value of 5 to 10 (3 to 6 per cent of theory) was obtained; when treated for 16 hours with the reagent made by the reaction of sodium with tertiary butyl alcohol, the result was 67 (40 per cent of theory). Smith (4) obtained low saponification values for methyl abietate and ethyl abietate when he saponified them in ethyl and n-butyl alcohol.

A method involving the heating of samples with alcoholic potassium hydroxide solution in a sealed glass tube would not constitute a satisfactory routine method even if the attack on the glass by the alkali could be avoided. After considerable amount of experimental work, the tertiary

butyl alcohol was replaced by cyclohexanol, the boiling point of which is 73° C. higher and which is almost equally stable in the presence of alkali. The insolubility of sodium cyclohexanolate in cyclohexanol was overcome by the addition of methanol, which is ultimately removed by boiling. The following conditions for effecting quantitative saponification of very difficultly saponifiable materials seemed most appropriate:

- (1) Use of approximately 0.6 *N* sodium methylate in methanol and cyclohexanol as a reagent. This is a clear, homogeneous, reasonably stable solution which attacks glass only slightly.
- (2) Use of an oil bath at 150° C., instead of a hot plate, in order to prevent local overheating. This high temperature accelerates the saponification.
- (3) Use of a nitrogen stream to prevent oxidation of the sample or the reagent.
- (4) Complete removal of the methanol used in preparing the reagent. This is done in order to have a sufficiently high reaction temperature.
- (5) Reaction for a 16-hour period.
- (6) Reaction in the presence of a slight amount of moisture.

TABLE I. SAPONIFICATION OF METHYL ABIETATE

Detn. No.	Weight of Sample Grams	Weight of Reagent Grams	<i>N</i> Alkali Consumed Cc.	Excess Reagent Used %	Saponification Value Found
1	0.5261	9.184	1.650	283	176.0
2	0.5516	9.398	1.746	271	177.5
3	0.5012	8.607	1.579	275	176.8
4	0.5297	9.662	1.675	297	177.4
7	0.9495	9.413	2.990	117	176.7
8	0.9917	9.647	3.112	113	176.1
9	0.9830	9.406	3.104	109	177.2
10	1.0130	9.693	3.173	110	175.8
				Av. Theory	176.7 177.4

Kolthoff and Furman (6) discuss the effect of the presence of water in the saponification reaction when sodium alcoholate is used as a reagent, giving references to articles where water is considered essential to the reaction (10) and also where even traces of it are considered harmful (2). Pardee, Hasche, and Reid (11) added 0.5 cc. of water to each flask in order to facilitate the saponification reaction. For carefully purified methyl abietate, some of the writers' saponification results, obtained under the above conditions in the absence of water, were 67.9, 99.6, 109.2, 97.7, 140.3, and 97.9. In two experiments made under exactly the same conditions except that 0.5 cc. of water was added, the flasks were very badly attacked by the free alkali but the results were 164.0 and 160.3, respectively. In all subsequent determinations water was added in the form of vapor by passing a slow current of nitrogen first through a wash bottle containing water and then through the reaction flasks. Under these conditions, the glass was not attacked and yet the saponification was complete, as shown by the satisfactory results in Table I.

## Apparatus

An oil bath which will maintain a constant temperature of about 150° C. for long periods without requiring attention. An apparatus consisting of two flat-bottomed concentric steel pans, differing both in depth and diameter, which were welded together and provided with a long pipe to serve as a condenser, has proved highly satisfactory for this purpose. The space between the pans contains about 3 liters of a suitable liquid—e.g., a mixture of commercial pinene and dipentene. An ordinary large oil bath provided with a device for maintaining a constant temperature would be equally satisfactory.

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So-called acetylation flasks fitted with condensers through 25-mm. standard-taper ground-glass connections. The condensers are nearly filled with water and have their water inlets and outlets capped. Two small tubes enter the top of the condenser through a rubber stopper, one extending just through the stopper (short inlet) and one extending through the condenser and about 2 cm. below its lower end (long inlet). This apparatus is shown in Figure 1.

Bailey weight buret.

### Reagents

1. Solution of sodium methoxide in methanol and cyclohexanol, containing approximately 0.6 cc. of *N* alkali per gram. This is prepared as follows: Add approximately 9.3 grams of sodium to 500 cc. of cyclohexanol, attach a reflux condenser, and add 250 cc. of absolute methanol in small portions. Reflux the solution overnight in order that the sodium methoxide may react completely with any esters which may be present as impurities. Cool, and preserve the reagent in a tightly stoppered bottle.
2. Sulfuric acid, approximately 0.1 *N*.
3. Sodium hydroxide solution, approximately 0.1 *N*.
4. 1 per cent alcoholic solution of phenolphthalein.
5. 1 per cent alcoholic solution of thymol blue.
6. Absolute alcohol, neutralized to phenolphthalein end point.
7. Moist nitrogen.

### Procedure

Weigh samples of suitable size (approximately 1 gram in the case of abietic acid esters) into acetylation flasks. The viscous esters may best be placed in the flasks by means of a stirring rod.

Fill the Bailey weight buret with reagent 1 and place weighed portions of about 10 cc. in each flask. Attach condensers to the flasks, and place the flasks in the oil bath at about 150° C. Pass a slow stream of moist nitrogen into the short inlets of the condensers for 30 minutes. This operation, performed in the hood because of methanol vapor, completely removes the methanol from the flasks. The methanol, along with a slight amount of cyclohexanol, is volatilized and forced out of the condenser through the long tubes, without having an opportunity to condense. Then rearrange the tubing connections and pass the moist nitrogen into the flasks through the long inlet tubes very slowly overnight. This causes the reaction to take place in an atmosphere free of oxygen and carbon dioxide. After bubbling through a wash bottle of water, the nitrogen stream is divided into four streams, each passing through four 1-mm. capillary tubes which are all of the same length (about 20 cm.) and then into the appropriate inlets at the tops of the condensers.

After they have been heated overnight, remove the reaction flasks from the bath and separate them from the condensers. Add 50 cc. of absolute alcohol, previously neutralized to the phenolphthalein end point, to each flask at once. If the reaction mixture does not dissolve completely in the alcohol, attach the flasks to Allihn condensers through which water is flowing and heat on a hot plate until solution is complete.

Titrate the solutions with 0.1 *N* sulfuric acid, using phenolphthalein as the indicator, and add enough 0.1 *N* alkali to make the solutions slightly alkaline. Add fragments of silicon carbide or porous plate to prevent bumping and boil the solutions for 30 minutes. This operation serves to hydrolyze completely any material present that can yield additional free alkali. Allow the solutions to cool, and titrate them with 0.1 *N* sulfuric acid and then to final end points with 0.1 *N* alkali.

When this drastic saponification method is applied to dark-colored substances, it is preferable to use 0.5 cc. of a 1 per cent alcoholic solution of thymol blue as indicator and to make the titrations with the aid of a hand spectroscope.

The concentration of the reagent should be determined under the same conditions as those which prevail in an analysis. If the reagent was properly stabilized, the concentration found will be substantially the same as that obtained if one titrates a sample of the reagent, without overnight heating, in the manner outlined above.

### Calculation

$$\frac{\left[ \begin{array}{l} (\text{Grams of reagent used} \times \text{cc. of } N \text{ alkali per} \\ \text{gram}) + (\text{cc. of NaOH} \times \text{normality factor}) - \\ (\text{cc. of H}_2\text{SO}_4 \times \text{normality factor}) \end{array} \right] \times 56.1}{\text{Grams of sample}} = \text{saponification value}$$

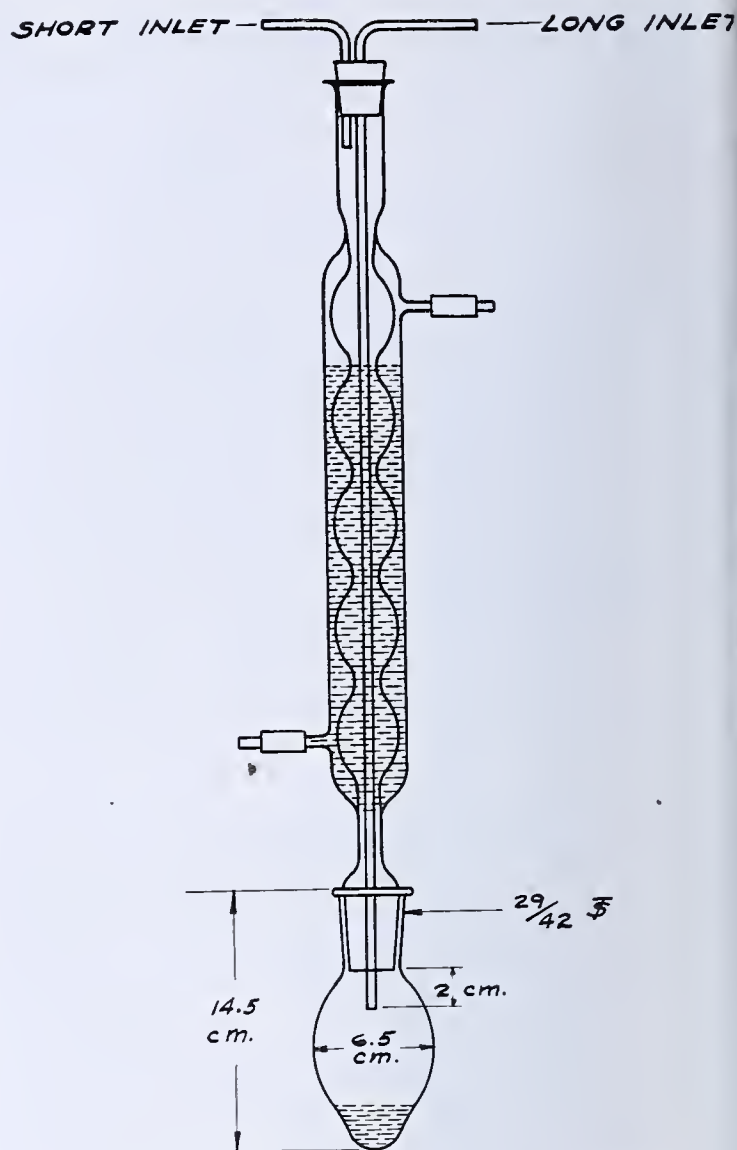


FIGURE 1. DRASTIC SAPONIFICATION APPARATUS

The specimen of methyl abietate which was used in the work had an acid number of 0.9. Determinations by the Zeisel method showed that it contained 9.77 per cent of  $\text{OCH}_3$  (theory, 9.81 per cent  $\text{OCH}_3$ ). Its density was 1.0442  $20^\circ/4^\circ$ , its index of refraction at  $20^\circ$  was 1.5336, its optical rotation was  $-45.6^\circ$ , and its thiocyanogen number was 93.

When the drastic saponification method was applied to specimen of commercial methyl abietate, the saponification numbers obtained were 164.6 and 165.7. The average of the values, 165.2, is 93.1 per cent of the theoretical. This specimen had previously been found to contain 9.09 per cent  $\text{OCH}_3$  (Zeisel method), which indicates a purity of 92.7 per cent. The saponification numbers (drastic method) *n*-butyl abietate were determined after a total of 16 and 40 hours' heating, respectively, with the following results:

16 hours	133.3, 133.3
40 hours	133.4, 135.2

Although these results indicate a purity of only 85 per cent they furnish additional evidence as to the validity of the method. Furthermore, the authors' saponification method gives concordant results when it is applied to other esters of abietic acid.

The drastic saponification method yields the theoretical saponification number—i. e., 185.8—when it is applied to pure recrystallized abietic acid. When applied to rosin the new reagent presumably reacts completely with all esters and anhydrides present.



TABLE II. SAPONIFICATION OF WOOD ROSIN

	FF Wood Rosin	I Wood Rosin
Acid No.	155.2	164.7
Saponification No. (usual method)	163.9	171.0
Saponification No. (drastic method)	173.0, 173.8	174.0, 173.8

TABLE III. LOSS IN WEIGHT OF PYREX FLASKS USED IN SAPONIFICATION DETERMINATIONS

Time of Heating Hours	Loss in Weight of Flasks	
	Flask 1 Mg.	Flask 2 Mg.
1	1.2	0.9
20	1.3	1.0
40	3.1	3.0
2	1.1	0.9
20	1.0	1.4

The relatively slight attack of the reagent on the Pyrex glass flasks is shown by the results in Table III.

Unfortunately, an ester of abietic acid which is commercially important, ester gum—i. e., the glycerol ester—cannot be analyzed by the method which has been devised because glycerol itself reacts with sodium methoxide to form monosodium glyceroxide and perhaps also some disodium glyceroxide (9). The writers do not know how these compounds behave on prolonged heating at 150° C., but evidence has been obtained which shows that a variable loss of alkalinity occurs when the saponification reagent is heated with glycerol. This naturally tends to make the results variable and too high. With the exception of ester gum, and presumably also the glycol ester of abietic acid and other glycerol and glycol esters, this method appears to be applicable to all difficultly saponifiable esters. Obermüller (10) was not troubled by a reaction between glycerol and sodium ethoxide, but presumably his saponifications were made at a much lower temperature—viz., the boiling point of ethanol. Kogan (5) analyzed ester gum by determining the difference between saponification numbers obtained with 0.5 N and 4 N potassium hydroxide.

The accuracy and precision of this method are both about

1 per cent when it is applied to reasonably light-colored products.

### Summary

A saponification method which is considerably more drastic than any heretofore suggested is recommended for the analysis of natural and synthetic products containing difficultly saponifiable esters. This method consists in the use of sodium methoxide in methanol and cyclohexanol, the removal of the methanol, and the heating of the reaction mixture in an oil bath at 150° C. for 16 hours in a current of moist nitrogen. The method has been applied to the quantitative saponification of pure methyl abietate and to the analysis of various impure abietic acid esters. It cannot be used in the presence of glycerol derivatives and presumably not in the presence of glycol derivatives.

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## The Determination of Water in Alcohol

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IN A STUDY of methods for determining the water content of oil sands, a method was developed which may be applied to the determination of water in alcohol, and possibly in other substances as well. It is a modification of methods which have been used for some time (1, 2, 3), but is felt to be somewhat more rapid and to require simpler equipment. It is an application of the fact that in the presence of certain organic liquids such as kerosene, carbon tetrachloride, xylol, etc., water and alcohol are only partially miscible. In the references cited the water content was determined by measuring the temperature at which cloudiness, caused by phase separation, occurred. The method presented here does not depend upon a temperature effect, but upon the amount of water required to titrate a given volume of liquid.

### Description of Method

Ethyl alcohol and carbon tetrachloride are miscible, but water is insoluble in carbon tetrachloride. If, then, carbon

tetrachloride is added to an alcohol-water mixture containing sufficient water, there will be a separation into two distinct layers, the act of separation producing initially a definite cloudiness throughout the liquid.

If 10 ml. of absolute alcohol are mixed with 10 ml. of carbon tetrachloride and titrated with water, an appreciable quantity of water (2.03 ml. at 25° C.) must be added before the appearance of cloudiness. If the alcohol already contains some water a smaller volume of water will be required to titrate. The difference between the amount of water required to titrate 10 ml. of absolute alcohol and that required to titrate 10 ml. of alcohol solution containing a given quantity of water represents the amount of water contained in the alcohol. Since a 10-ml. sample of alcohol solution contains less than 10 ml. of alcohol, the volume of contained water is not simply the difference between the titration value for this solution and for 10 ml. of pure alcohol, but is slightly less than this.

The simplest way of determining the titration value for



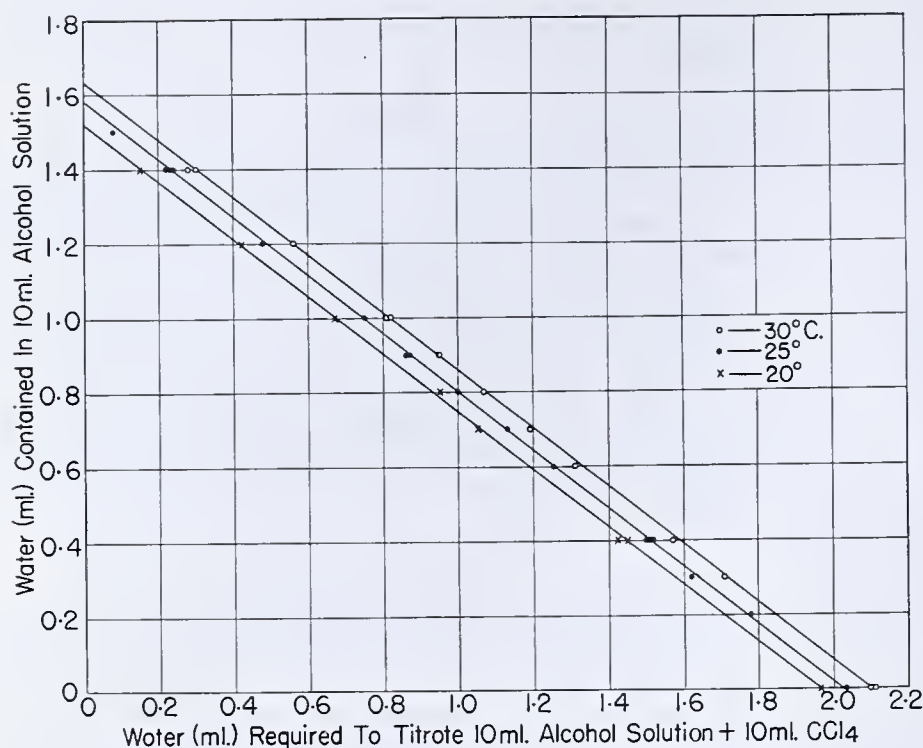


FIGURE 1. CALIBRATION CURVES

various concentrations of water in alcohol appeared to be by the establishment of an empirical calibration curve. This curve was obtained by titrating 10-ml. portions of alcohol solutions containing accurately known quantities of water. To each 10 ml. of alcohol solution 10 ml. of carbon tetrachlo-

ride were added before titrating. For this purpose 10-ml. pipets were used and the water titration was made from a 10-ml. buret graduated to 0.05 ml. If the alcohol solution contains more than about 15 per cent of water, new calibration curves will have to be established using a smaller quantity of carbon tetrachloride.

Since this titration is very sensitive to temperature, three calibration curves (Figure 1) were established at 20°, 25°, and 30° C. Interpolation between these curves permits the titration to be made at any ordinary room temperature. The volume of water required to titrate is the abscissa, while the ordinate is the volume of water contained in a 10-ml. portion of alcohol solution. The fact that the curves are parallel straight lines makes the interpolation for intermediate temperatures very simple. The results obtained by this method are accurate to within  $\pm 2$  per cent. The curves are valid, of course, only for ethyl alcohol and carbon tetrachloride. Other curves may be established for other alcohols and organic liquids.

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RECEIVED June 23, 1938.

## Elimination of Surface Tension Effects in Specific Gravity Measurements

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IN THE measurement of specific gravity of water and aqueous solutions of high surface tension by means of specific gravity balances, considerable uncertainty may be introduced owing to surface tension effects that act on the wire supporting the plummet. Similar effects may be encountered with analytical balances, in determining specific gravity by the displacement method.

The effect of nonuniform wetting is to introduce a resistance to motion of the plummet, making it impossible to obtain accurate values. If the balance point is approached by raising the plummet, specific gravity values are lower than those obtained when the motion of the plummet is in the opposite direction.

The magnitude of these effects is indicated by the following measurements on distilled water, taken on the Becker chainomatic balance:

Plummet Motion	Observed Specific Gravity at 23.0° C.	Specific Gravity at 20°/20°
Downward	0.9999	1.0004
	1.0000	1.0005
Upward	0.9990	0.9995
	0.9989	0.9994

Whereas the above pairs of values differ materially, their average gives a good value for water, although this is more or less fortuitous, as reproducible wetting of the plummet wire

does not always occur. As an example of this effect, the following measurements on a dilute salt solution are given:

Plummet Motion	Observed Specific Gravity at 23.0° C.	Specific Gravity at 20°/20°
Downward	1.0008	1.0013
	1.0013	1.0018
	1.0009	1.0014

Such effects as those illustrated above make it apparent that accurate values of specific gravity are difficult to obtain and require tedious repetition of measurements.

In instructions for use of specific gravity balances, the writer is not aware that any precautionary warnings as to surface tension effects are given, or any provision made for assuring reproducible wetting of the wire.

In order to avoid these difficulties and to secure rapid and accurate measurements of specific gravity, the writer has adopted the simple expedient of adding a minute amount of a water-soluble, surface-active material to the liquid whose specific gravity is to be determined. Since these liquids may include various brines or other aqueous solutions, as well as distilled water, the addition agent must be of a type that is non-reactive with the components of such solutions. A class of materials that admirably meets these requirements consists of the sulfonated or sulfated higher alcohols, typified by sodium lauryl sulfate. There are, of course, a number of similar



and equivalent materials that may be used for the purpose and that exert a large lowering effect on surface tension when used in very small quantities. These addition agents also assure complete and reproducible wetting of the plummet wire.

The procedure employed in using these materials is to add a small drop of a dilute solution (approximately 1 per cent) of sodium lauryl sulfate to the surface of the aqueous solution in the measuring cylinder, after immersion of the plummet of the balance. In this way, diffusion of the addition agent into the aqueous solution is minimized and its effect on the specific gravity of the solution will be negligible. As an example of the beneficial effects of this procedure, the following measurements on the same distilled water sample as that previously cited are given:

Observed Specific Gravity at 23.0° C.	Specific Gravity at 20°/20°
0.9996	1.0001
0.9995	1.0000

The values obtained are independent of the direction of motion of the plummet and are reproducible to the limits of

sensitivity of the balance. The behavior of the balance is very different after addition of the surface tension depressant. The short fast oscillations previously obtained with water are replaced by the long slow swings characteristic of a slightly damped analytical balance. The readings can be taken by balancing to zero in the usual manner, or can be obtained by the method of swings.

As further proof that balancing difficulties are due to surface tension and wettability effects on the plummet wire, it is only necessary to examine the water surface by oblique illumination. With pure water, the meniscus at the wire can be observed to move in the same direction as the plummet, as it is raised or lowered. After addition of the surface tension depressant, the plummet can be raised or lowered at will without visible alteration of the meniscus at the wire, thereby indicating its complete wettability.

The operating procedure given above has been adopted as standard in the author's laboratory and is recommended as being of material assistance in measurements of specific gravities of liquids of medium to high surface tension.

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# Determination of Ortho-, Pyro-, and Metaphosphoric Acids

## By Colorimetric pH Titrations

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THE recent offering in commercial quantities of anhydrous phosphoric acids has occasioned interest in the compositions and hydration characteristics of such compounds (?). These acids, made by the partial hydration of phosphoric anhydride, contain from 73 to 88 per cent of phosphorus pentoxide. They range from sirupy to thick viscous liquids; impurities are negligible. This paper describes a method for the determination of their compositions in terms of ortho-, pyro-, and metaphosphoric acid by the use of colorimetric pH titrations.

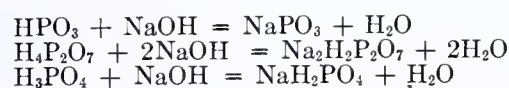
For the determination of the three phosphoric acids, Aoyama (2) neutralized with sodium hydroxide solution, added a measured excess of silver nitrate and enough alcohol to make the content 50 per cent, and determined the excess silver after removal of the precipitated silver phosphates by filtration. Dworzak and Reich-Rohrwig (4) revised the procedure by introducing a two-step neutralization. The solution was first neutralized to phenolphthalein indicator, and then, after treating with silver nitrate and alcohol followed by filtration, it was again neutralized using 0.1 *N* sodium hydroxide until the newly formed silver precipitate showed a distinct gray tint due to the precipitation of silver oxide which is formed when all the phosphate is precipitated. After filtration, the excess silver was determined as by Aoyama. The precipitated silver phosphates were treated with hydrogen sulfide (2) or hydrochloric acid (4) to form the phosphoric acids which, after separation by filtration, were titrated with sodium hydroxide to both the methyl orange and phenolphthalein end points. From these two titrations and the silver determination the amounts of ortho-, pyro-, and metaphosphoric acids were calculated.

These methods of determination may be greatly simplified,

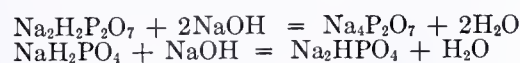
especially for anhydrous acids as mentioned above, if the silver determination is replaced by measurement of the sodium hydroxide required to neutralize in the presence of an excess of silver, while the accuracy and precision of the acidimetric titrations may be greatly increased by making allowance for the differences between the equivalence points of the ortho- and pyrophosphates.

### Outline of Proposed Method

For titration purposes, meta-, pyro-, and orthophosphoric acids are considered, respectively, as mono-, di-, and tribasic acids which may be quantitatively neutralized in three steps. For the determination a portion of the anhydrous acid, carefully diluted with ice water to avoid hydration, is titrated under stated conditions with standard sodium hydroxide solution to pH 4.4 (a provisional value) at which point the reactions are:



By continuing the titration to pH 8.8 (a provisional value) in the presence of a suitable quantity of added sodium nitrate to reduce hydrolysis, additional hydrogens of ortho- and pyrophosphoric acids are neutralized, giving:



If at this point an excess of silver nitrate is added, normal silver phosphates are subsequently precipitated, and the remaining hydrogen of the orthophosphoric acid can be titrated with sodium hydroxide, using methyl red as indicator.



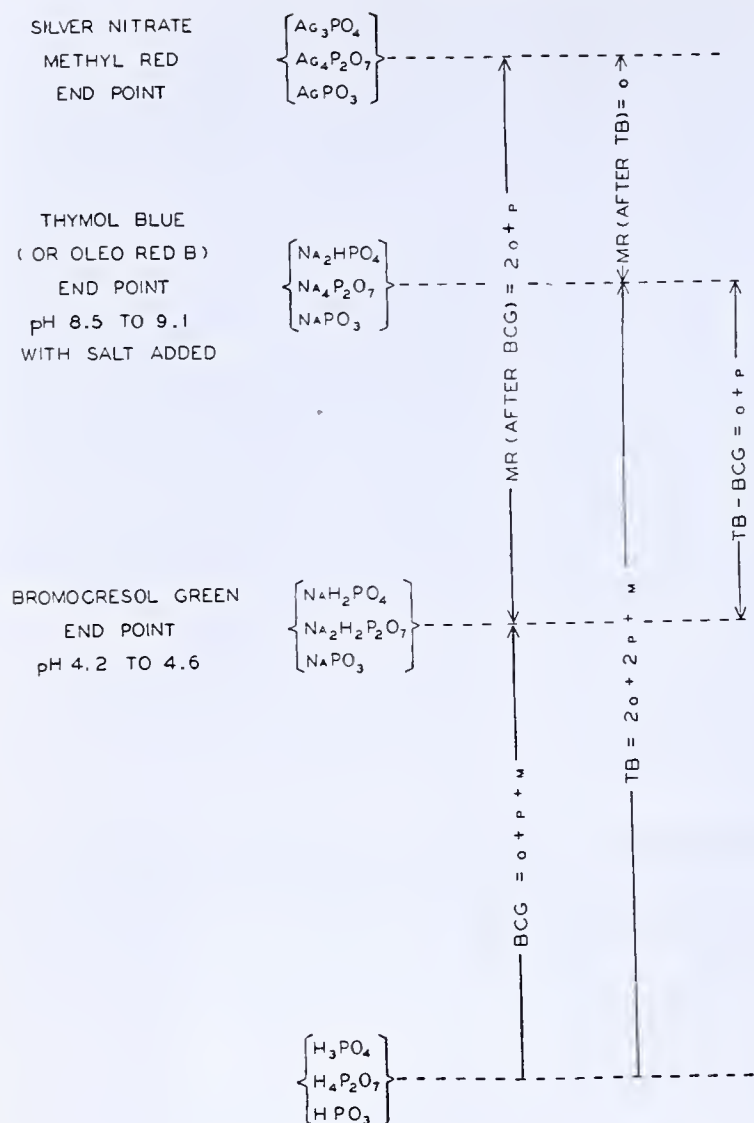
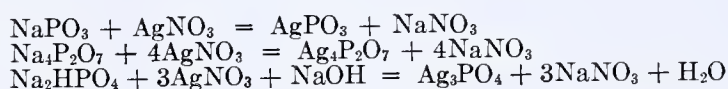


FIGURE 1. RELATIONS OF TITRATION VALUES TO ORTHO-, PYRO-, AND META- $\text{P}_2\text{O}_5$  CONTENTS OF PHOSPHORIC ACIDS



In each of the above titrations two moles of sodium hydroxide are equivalent to one mole of phosphorus pentoxide whether present as ortho, pyro, or meta. From the three titrations, the three components, expressed as ortho-, pyro-, and meta- $\text{P}_2\text{O}_5$ , may be found by two successive subtractions.

Because of indicator conflicts, the above sequence of titrations is not followed in actual practice. Instead, two equal portions of the sample are titrated, one with bromocresol green indicator to pH 4.4, the other with thymol blue (or oleo red B) indicator to pH 8.8 in the presence of added sodium salt. At these equivalence points, silver nitrate may be added to either solution for the final titration with methyl red indicator. Since the methyl red end point is perhaps better seen in the solution containing bromocresol green, use of this solution is described in the procedure below. The methyl red titration equations are then:

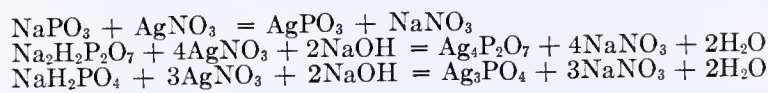


Figure 1 shows the products present at the different end points and the relations of titration values to the ortho-, pyro-, and meta- $\text{P}_2\text{O}_5$  content.

The provisional values of pH 4.4 and 8.8 used in the above explanation are subject to further definition depending upon the relative amounts of ortho- and pyrophosphoric acids present. Under the conditions of test, the equivalence point of monosodium orthophosphate is pH 4.6 while that of sodium acid pyrophosphate is 4.2. The equivalence point of disodium orthophosphate is likewise pH 8.5, while that of tetrasodium pyrophosphate is 9.1. The end-point values for mixtures will lie between the equivalence points of the pure salts. If the relative proportions of ortho- and pyrophosphoric acids are roughly known, the desired end-point values may be obtained directly from a linear interpolation scale such as Figure 2. If the proportions are unknown, buret readings should be taken at pH 4.2, 4.4, and 4.6 in the bromocresol green titration, and at pH 8.4, 8.6, 8.8, 9.0, and 9.2 in the thymol blue titration or at least at such pH values as will embrace the end point. The final titration volumes can subsequently be determined when the exact end points have been ascertained from a nomograph such as Figure 3. Since the methyl red titration may, on option, be performed after the thymol blue (or oleo red B) titration, two methyl red titration scales are shown in this figure.

When the polybasic acid present is chiefly pyrophosphoric, as foretold by a white, not yellow, precipitate upon the addition of silver nitrate, the substitution of LaMotte oleo red B indicator for thymol blue is advantageous, as the color intervals at pH 8.8 to 9.2 are then more distinct. In this event, readings need not be obtained at pH 8.4 and 8.6. Conversely, when the precipitate with silver nitrate is bright yellow, the titration need not be extended to include pH 9.0 and 9.2.

### Apparatus and Solutions

Titration are made in 250-cc. pH titrating flasks, Almquist type, marked to indicate the 100-cc. level. These flasks have side tubes of the same dimensions as LaMotte color standard tubes. The following freshly standardized LaMotte color standards are used: pH 4.2, 4.4, and 4.6, bromocresol green; pH 8.4, 8.6, 8.8, 9.0, and 9.2, thymol blue; and pH 8.6, 8.8, 9.0, and 9.2, oleo red B.

STANDARD SODIUM HYDROXIDE, 0.1408 N; 1 cc. = 0.01 gram of  $\text{P}_2\text{O}_5$ . Prepare a carbonate-free solution from centrifuged sodium hydroxide liquor (1). Standardize against pure benzoic acid.

SILVER NITRATE SOLUTION, 0.85 N; 144 grams of pure crystals per liter. Ten cubic centimeters are equivalent to 0.2 gram of ortho- $\text{P}_2\text{O}_5$ , 0.3 gram of pyro- $\text{P}_2\text{O}_5$ , or 0.6 gram of meta- $\text{P}_2\text{O}_5$ . Use in such quantities that all phosphate (and chloride if present) will be precipitated and at least 5 cc. in excess be present.

BROMOCRESOL GREEN INDICATOR, 0.4 per cent solution. Dissolve 0.4 gram of the dry indicator in 4.1 cc. of 0.1408 N sodium hydroxide and a few cubic centimeters of alcohol. Dilute with water to 100 cc.

THYMOL BLUE INDICATOR, 0.4 per cent solution. Dissolve 0.4 gram of the dry indicator in 6.1 cc. of 0.1408 N

FIGURE 2. pH END POINTS FOR VARYING ORTHO:PYRO  $\text{P}_2\text{O}_5$  RATIOS

B C G END POINT	RATIO ORTHO:PYRO		T B END POINT
	4.6	100:0	8.5
4.5		80:20	8.6
		60:40	8.7
4.4		40:60	8.8
4.3		20:80	8.9
		0:100	9.0
4.2			9.1

sodium hydroxide and 5 to 10 cc. of water. Dilute with water to 100 cc.

METHYL RED INDICATOR, 0.2 per cent solution. Dissolve 0.2 gram of the dry indicator in 60 cc. of alcohol. Dilute with water to 100 cc.

OLEO RED B INDICATOR, 10 times normal strength. Mix 20 cc. of 60 per cent alcohol with 40 cc. of LaMotte oleo red B strong solution, 15 times normal strength.



# Procedure for Anhydrous Phosphoric Acids

**PREPARATION OF SOLUTION.** Set up a 400-cc. beaker containing about 200 cc. of ice water stirred with a motor stirrer. Slowly pour the sample, about 10 grams weighed by difference, into the beaker in such a manner as to avoid local overheating. When well mixed, transfer to a 500-cc. volumetric flask, add water to mark, and remix. Transfer a 25-cc. aliquot (containing 0.3 to 0.4 gram of phosphorus pentoxide) to each of two pH titrating flasks. Make the titrations below without delay.

**BROMOCRESOL GREEN TITRATION.** To one aliquot add 0.5 cc. of 0.4 per cent bromocresol green indicator. Titrate with standard sodium hydroxide solution until pH 4.2 is approached, then dilute to 100-cc. volume. Continue the titration, recording the volumes of sodium hydroxide required to bring the pH to 4.2, 4.4, and 4.6 when compared against color standards.

**METHYL RED TITRATION.** To the solution above at 4.6 pH, add 25 cc. of 0.85 *N* silver nitrate solution and shake briskly to coagulate the precipitate. Add 0.5 cc. of 0.2 per cent methyl red indicator. Titrate with standard sodium hydroxide until the pink color of the liquid is just discharged. When near the end point, shake briskly after each sodium hydroxide addition, then allow the precipitate to subside momentarily in order that the exact point of color change may be clearly seen. Shaking is important, as otherwise the color of the solution may be muddy.

**THYMOL BLUE TITRATION.** To the other aliquot add 0.5 cc. of 0.4 per cent thymol blue indicator (or 0.5 cc. of oleo red B indicator, 10 times normal strength, when pyrophosphoric acid predominates) and 20 grams ( $\pm 1$  gram) of neutral sodium nitrate (or 14 grams of sodium chloride). Titrate with standard sodium hydroxide until pH 8.4 is approached, then dilute to 100 cc. Continue the titration, recording the volumes of sodium hydroxide required to reach pH 8.4, 8.6, 8.8, 9.0, and 9.2 as shown by color standards. Subtract from each volume a titration blank (usually 0.1 cc.) found by titrating to pH 8.8 a solution of 20 grams of sodium nitrate crystals in sufficient water to make 100-cc. volume.

**CALCULATIONS.** From the pH nomograph (Figure 3) determine the exact end-point values for the composition of the acid under test. Using these values, determine by interpolation the volumes of sodium hydroxide required to reach the two end points. Correct the methyl red titration volume for any shortage due to starting the titration at pH 4.6. From the three corrected volumes designated below as *BCG*, *TB*, and *MR*, calculate the composition:

$$\begin{aligned} BCG \times 0.01 &= \text{grams of total } P_2O_5 (o + p + m) \\ (TB - BCG) \times 0.01 &= \text{grams of } P_2O_5 (o + p) \\ [MR - (TB - BCG)] \times 0.01 &= \text{grams of } P_2O_5 (o) \end{aligned}$$

**EXAMPLE.** A 9.7596-gram sample of acid (0.4880 gram in each aliquot) gave the following titrations:

Bromocresol green	37.02 cc. to pH 4.2
	37.20 cc. to pH 4.4
	37.38 cc. to pH 4.6
Methyl red (from pH 4.6)	53.41 cc. to MR end point
Thymol blue (less blank)	72.35 cc. to pH 8.4
	72.70 cc. to pH 8.6
	73.00 cc. to pH 8.8
	73.35 cc. to pH 9.0
	73.70 cc. to pH 9.2

Lay a straight edge on the pH nomograph connecting 53.41 on the left-hand scale (since the methyl red titration was run on the bromocresol green solution) with 35.80, 73.00 - 37.20 on the right-hand scale. This cuts the pH scale at 4.4 and 8.8. Using these end points, the results become:

BCG titration	37.20 cc. to pH 4.4
MR titration (from pH 4.4)	53.41 + (37.38 - 37.20) = 53.59 cc.
TB titration (less blank)	73.00 cc. to pH 8.8

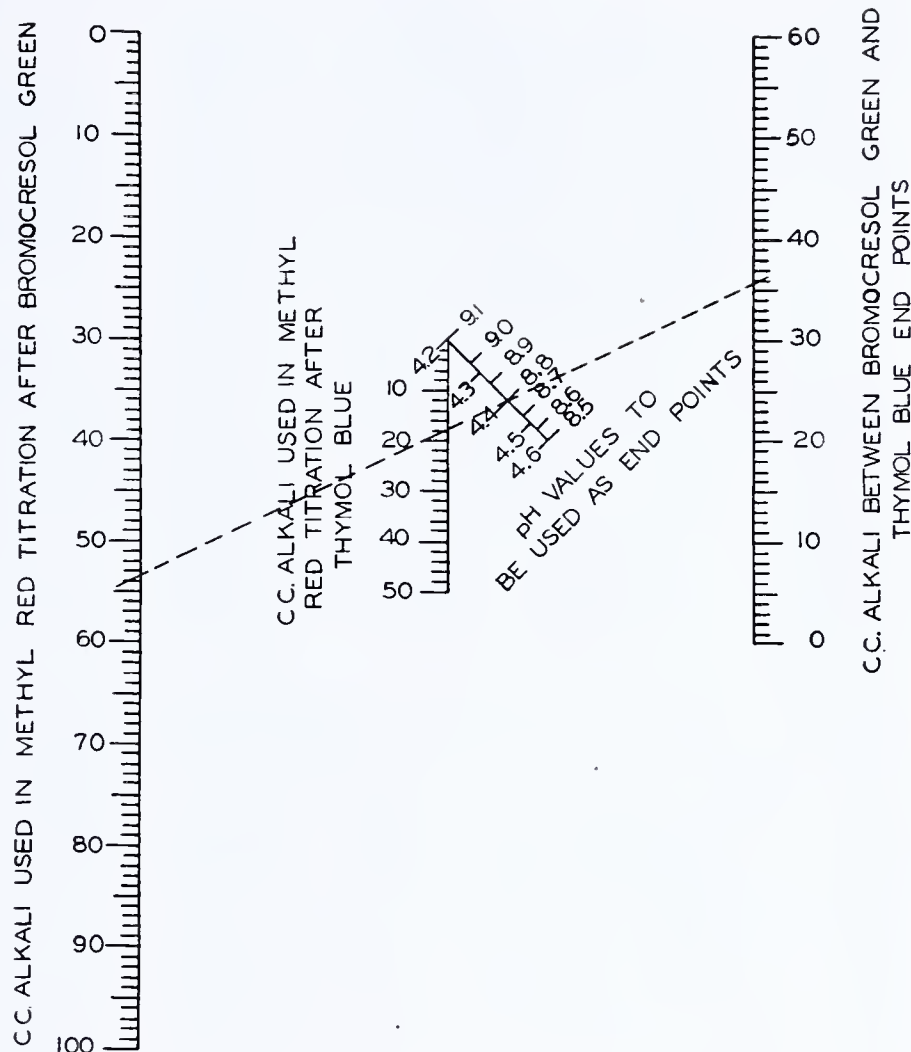


FIGURE 3. pH NOMOGRAPH FOR FINDING END POINTS FROM TITRATIONS

Using these corrected volumes:

$$\begin{aligned} 37.20 \times 0.01 &= 0.3720 \text{ gram of total } P_2O_5 (o + p + m) \\ (73.00 - 37.20) \times 0.01 &= 0.3580 \text{ gram of } P_2O_5 (o + p) \\ [53.59 - (73.00 - 37.20)] \times 0.01 &= 0.1779 \text{ gram of } P_2O_5 (o) \end{aligned}$$

By subtraction: Meta- $P_2O_5$  = 0.0140 gram and pyro- $P_2O_5$  = 0.1801 gram.

Converting these  $P_2O_5$  values to acids we have 3.2 per cent of meta-, 46.3 per cent of pyro-, and 50.3 per cent of orthophosphoric acid.

## Advantages of the Method

Although neutralization with sodium hydroxide after treatment with silver was employed by Dworzak and Reich-Rohrwig (4), no use was made of the amount of sodium hydroxide so required. In the present method, the end point of the neutralization is determined by methyl red indicator which is satisfactory even in the presence of the other specified indicators, instead of by the less easily detected appearance of silver oxide. The sodium hydroxide required is then used in obtaining the orthophosphoric acid content. The addition of alcohol is unnecessary, since the solubility of silver metaphosphate in aqueous solution is then of no concern. In those methods (8, 10) for the analysis of mixtures of ortho- and pyrophosphates where calcium chloride has been used for precipitation, use has been made of the barium hydroxide or sodium hydroxide required after precipitation and heating to neutralize to phenolphthalein. The control of conditions to ensure a calcium phosphate of theoretical composition is, however, difficult.

Titrations with methyl orange and phenolphthalein indicators as previously performed are subject to inaccuracy be-



cause of the relatively slow pH changes in the neutralization of the phosphoric acids. The specifying of the indicators alone is insufficient; accuracy can be obtained only by careful pH measurements at the equivalence points (6). Furthermore, allowance should be made for the fact that the equivalence points of the ortho- and pyrophosphates do not coincide. In the present method, the equivalence points at a stated concentration are defined in terms of colorimetric pH, these equivalence points are at the sensitive section of the pH range of the specified indicators, and the addition of salt to reduce hydrolysis is prescribed in such a concentration that the equivalence points of tetrasodium pyrophosphate and of disodium orthophosphate are brought into definite proximity as shown in Figure 4. Moreover, a sliding scale of end points has been constructed for varying proportions of ortho- and pyrophosphoric acids. These features, in conjunction with the use of pH color standards, greatly increase the precision and accuracy of the acidimetric titrations. Since in the present method these titrations are done before the addition of silver nitrate, the filtration and treatment with hydrogen sulfide or hydrochloric acid to regenerate the free acids are unnecessary.

No color standard is used in determining the methyl red end point on account of the precipitate present in the solution. However, since the polybasic phosphoric acids have been precipitated by the silver, the titration is that of a strong acid, nitric, with a strong base giving a sharp break in pH at the end point. The break is so sharp that by using a low-resistance glass electrode the end point may be satisfactorily determined by potentiometric means with an electron beam sectrometer (9) which indicates only changes of e. m. f. on addition of titrating solution and does not determine pH values. The use of this instrument permits a more rapid determination, as no pauses during titration are required to view the indicator color, but is not a necessity in obtaining good titration values.

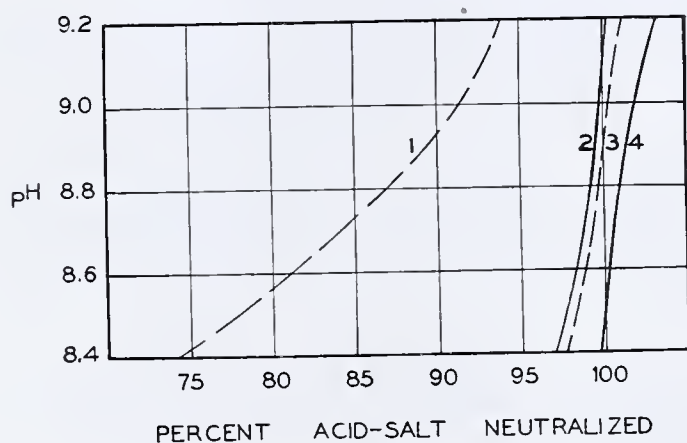


FIGURE 4. EFFECT OF SALT ON TITRATION CURVES AT THYMOL BLUE END POINT

1. Pyrophosphate, no salt added
2. Pyrophosphate, 20 grams of sodium nitrate per 100 cc.
3. Orthophosphate, no salt added
4. Orthophosphate, 20 grams of sodium nitrate per 100 cc

The method does not depend upon any selective precipitation reactions of the pyrophosphoric acid similar to the zinc (3, 5, 11) or the magnesium (4) methods which at times give low results (7) or fail entirely to give precipitates. To illustrate, an anhydrous acid containing 81 per cent of phosphorus pentoxide when diluted and neutralized to bromophenol blue indicator shows no precipitate upon the addition of zinc sulfate, while the present method shows a pyrophosphoric acid content of 64 per cent. In the present method, silver is used for precipitation but the compositions of the silver phosphates are immaterial so long as hydrogen ion is not included in the precipitate.

## Limitations of the Method

The end point values shown by Figure 3 are based on a concentration of 0.4 gram of phosphorus pentoxide per 100 cc. and cannot be accurately applied to concentrations differing widely from this. If titrations are desired at other concentrations, appropriate equivalence points must be first determined. If the titrations are made at temperatures more than 5° from 25° C., the given end-point values may be inaccurate.

TABLE I. RESULTS ON KNOWN MIXTURES

Grams of P <sub>2</sub> O <sub>5</sub> Taken			Grams of P <sub>2</sub> O <sub>5</sub> Found		
Ortho	Pyro	Meta	Ortho	Pyro	Meta
0.4000	0.0000	0.0000	0.4008	0.0012	
0.4000	0.0000	0.0000	0.4021	(-0.0017)	(-0.0001)
0.3200	0.0800	0.0000	0.3219	0.0794	
0.3000	0.1000	0.0000	0.3007	0.0990	0.0000
0.2000	0.2000	0.0000	0.2010	0.1986	0.0007
0.1333	0.2667	0.0000	0.1340	0.2660	
0.1000	0.3000	0.0000	0.1018	0.2974	
0.1000	0.3000	0.0000	0.0994	0.3019	(-0.0015)
0.0000	0.4000	0.0000	(-0.0003)	0.4006	
0.2400	0.0600	0.1000	0.2404	0.0591	0.1008
0.1500	0.1500	0.1000	0.1511	0.1502	0.0984
0.0750	0.2250	0.1000	0.0740	0.2255	0.0999
0.2000	0.0020	0.1980	0.2018	0.0016	0.1944
0.0000	0.2000	0.2000	0.0001	0.2028	0.1955

Weak acids or weak bases cannot be present in the sample, as their buffer action interferes with the titration values. Strong acids such as sulfuric, nitric, and hydrochloric or strong bases do not interfere with the ortho and pyro values, but the bromocresol green titration does not then represent the total phosphorus pentoxide. In this case an aliquot of the sample must first be hydrated to orthophosphoric acid and the total phosphorus pentoxide determined. The hydration may be accomplished by diluting the aliquot to 100 cc., adding 7 cc. of concentrated nitric acid, and then boiling steadily for 15 minutes. The acid solution is then nearly neutralized with 50 per cent sodium hydroxide solution, cooled, and accurately adjusted to pH 4.6 (at 100-cc. volume) as shown by bromocresol green color standard, silver nitrate solution is added in excess, and the solution is titrated with standard sodium hydroxide using methyl red indicator. In this titration 1 cc. of 0.1408 N sodium hydroxide is equivalent to 0.005 gram of phosphorus pentoxide. The ortho and pyro contents are calculated in the usual manner and meta obtained by difference.

Basic and metallic elements which give insoluble phosphates in the course of the thymol blue titration interfere in proportion to the amount present, giving high results for pyro and low results for ortho and meta. If the iron and aluminum content of the acid do not exceed 0.1 per cent each, the interference is negligible.

## Experimental

Since pure meta- and pyrophosphoric acids were not available for demonstration of the accuracy of the method by the titration of known mixtures, titrations were made on known mixtures of sodium ortho- and pyrophosphates acidified with sulfuric acid with and without the addition of sodium metaphosphate. The following salts were used:

Disodium phosphate and monopotassium phosphate, Sørensen grade.

Tetrasodium pyrophosphate crystals, obtained by three recrystallizations of a commercial grade of crystals.

Sodium metaphosphate made by fusing pure monosodium phosphate; the product was not obtained altogether free of pyrophosphate as shown by the pH 4.2 to 9.1 titration. Although some of the sodium hydroxide consumed may be caused by a very slight buffer action of the metaphosphate itself, this titration was calculated to pyro-P<sub>2</sub>O<sub>5</sub> and corrections were made on this basis where metaphosphate was used in known mixtures. By this calculation the titration is equivalent to 0.70 per cent of pyro-P<sub>2</sub>O<sub>5</sub>.

Since the amount of sulfuric acid added was not accurately



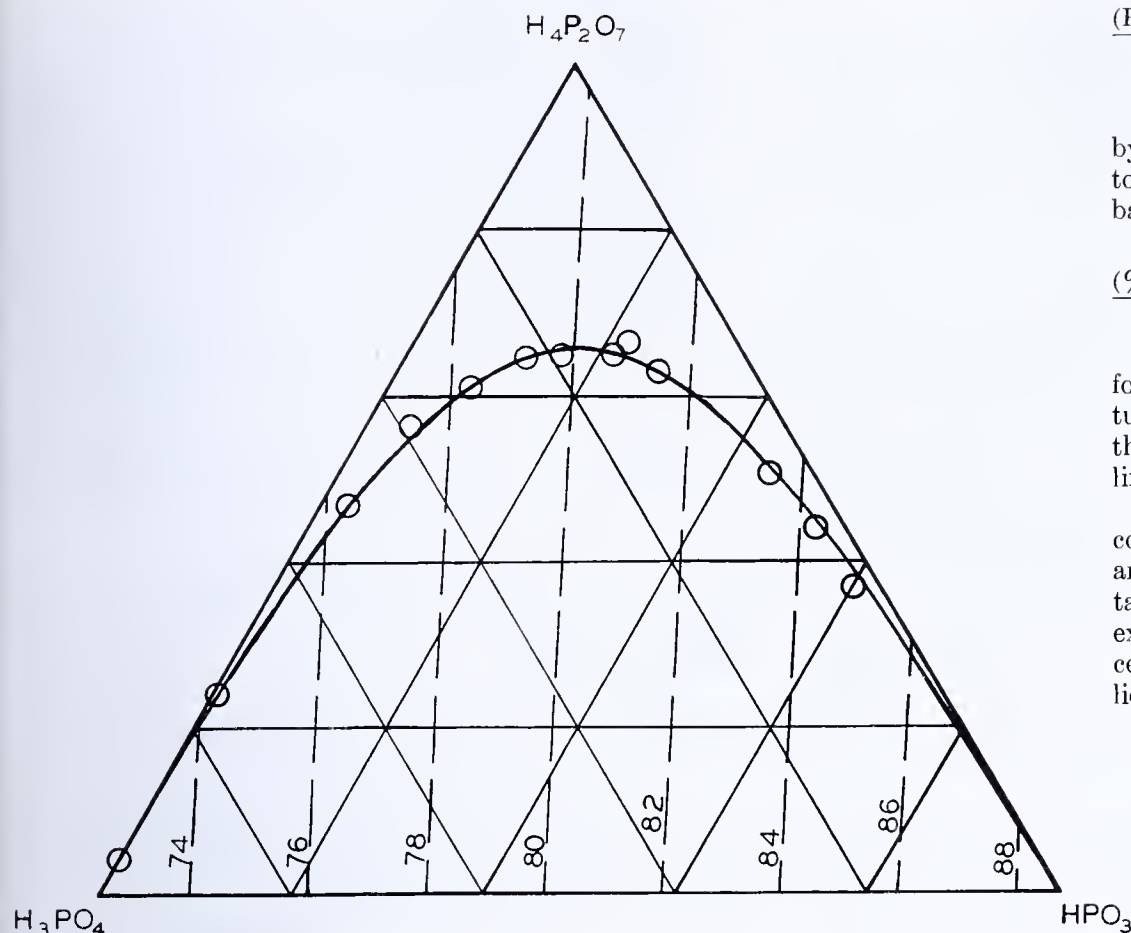


FIGURE 5. COMPOSITIONS OF ANHYDROUS PHOSPHORIC ACIDS

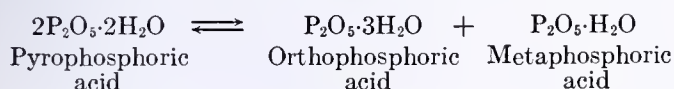
— Compositions given by equilibrium constant  
 ○ Compositions found by colorimetric pH titrations  
 - - - Lines of equal per cent  $P_2O_5$

known, the bromocresol green titration did not represent the total phosphorus pentoxide and this was necessarily obtained from a titration on a third aliquot after hydration to orthophosphate as described above. Metaphosphate was calculated by difference.

Table I shows the ortho-, pyro-, and (in experiments where the total phosphorus pentoxide was determined) meta- $P_2O_5$  found by colorimetric pH titrations on acidified known mixtures. The errors are greatest in the case of meta- $P_2O_5$  since this value involves titrations on three different aliquots. The average error for 9 determinations of meta- $P_2O_5$  is less than 0.4 per cent of the total  $P_2O_5$ . Owing to the occasional accumulation of experimental errors due to the interdependence of the three titrations, the accuracy of the method as a whole is difficult to define. As a general rule, however, the results should be accurate to  $\pm 0.4$  per cent.

### Hypothetical Polymerized Acids

In view of the numerous polymers and polyphosphoric acids which have been reported or hypothesized (7), the possible interference of such compounds in the present titration method is of importance. Since convenient means of identifying these compounds are lacking, a series of 13 anhydrous acids covering the range from 74 to 85 per cent of phosphorus pentoxide was analyzed. The results are shown by small circles on the trilinear chart, Figure 5. The distribution of these points suggested an equilibrium. In the absence of any data on the polymeric form of the acids we may write:



The equilibrium constant on a mole basis is:

$$\frac{(P_2O_5 \cdot 3H_2O) \cdot (P_2O_5 \cdot H_2O)}{(P_2O_5 \cdot 2H_2O)^2} = k = 0.06_9$$

Multiplying these concentrations by the respective molecular weights to convert to a weight per cent basis, this becomes:

$$\frac{(\% H_3PO_4) \cdot (\% HPO_3)}{(\% H_4P_2O_7)^2} = k' = 0.06_8$$

for liquid acids at room temperature. Compositions calculated from this constant are shown by a curved line on the trilinear chart.

At some phosphorus pentoxide contents, these equilibrium mixtures are metastable with respect to crystal forms at room temperature. For example, an acid containing 79.5 per cent of phosphorus pentoxide solidified on standing. Analysis of the solid, without removal of the adhering liquid, showed 2.0 per cent of ortho-, 96.7 per cent of pyro-, and 0.4 per cent metaphosphoric acid. Therefore the pure solid phase was doubtless pyrophosphoric acid. After melting and cooling to room temperature, analysis showed 21.1 per cent of ortho-, 65.1 per cent of pyro-, and 13.6 per cent of metaphosphoric acid in agreement with the equilibrium constant.

The existence of this equilibrium does not, however, preclude other reactions involving equilibrium concentrations of polymers and polyphosphoric acids (7). From the data available the conclusion is reached that any polymers which may be present have the same pattern of replaceable hydrogens in the titrations as the simple acids. For example, polymers of metaphosphoric acid behave like a monobasic acid. Polyphosphoric acids, if present, titrate as mixtures of ortho-, pyro-, and metaphosphoric acids.

These conclusions are justified by the results which show that (1) the total phosphorus pentoxide calculated from the bromocresol green titration agrees very closely with the total phosphorus pentoxide determined by hydration to orthophosphoric acid followed by molybdate precipitation and that (2) the sum of the three calculated components, ortho- pyro-, and metaphosphoric acid, agrees closely with the weight of sample taken. This latter fact is also proof that anhydrous acids, if carefully diluted and promptly titrated, do not undergo appreciable hydration during the test.

While the present titration method gives no information regarding the molecular structure of the acids present, it does show the amounts of phosphorus pentoxide associated with one, two, or three molecules of water which are designated as meta-, pyro-, and orthophosphoric acids, respectively, and represented for convenience by the simple formulas.

### Summary

The determination of ortho-, pyro-, and metaphosphoric acids in mixtures is accomplished by colorimetric pH titrations, aided by color standards and by a sliding scale of end-point values depending upon the proportions of ortho- and



pyrophosphoric acids present. The alkali required to neutralize the acidity resulting from the formation of normal silver orthophosphate is used as a measure of the orthophosphoric acid content. From analyses on samples of liquid anhydrous phosphoric acids containing 74 to 85 per cent of phosphorus pentoxide an equilibrium constant is calculated for the reaction  $\text{H}_4\text{P}_2\text{O}_7 = \text{H}_3\text{PO}_4 + \text{HPO}_3$ .

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## Determination of Age of Inks by the Chloride Method

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SEVERAL years ago the authors were called to the defense of a young man accused of cheating on a state bar examination. It was claimed that he had made additions to his examination book several months subsequent to the examination date. The additions had been examined by a well-known expert criminologist, who had used the chloride method of Turkel (2) and had found the chloride migration in some of the suspected additions less than in other ink on the same page of the examination book. The young man was, therefore, threatened with being forever disbarred from the practice of law.

The present authors observed that the alleged additions were made in a different color of ink from the body of the writing on the page under consideration. The question therefore arose as to whether the rate of chloride migration from all chloride-containing inks would be identical.

### Rate of Chloride Migration

Comparative tests were therefore made on various commercial inks, using the method previously reported (1). The document was immersed in a 2 per cent solution of silver nitrate, washed three times with distilled water, and developed with the photographic developer D72. This destroys the ink, but does not blacken the paper as permanganate does. The essential advantage of this process is its simplicity.

It was found that the rate of chloride migration does depend on the nature of the ink. In particular "Sanford's Royal Blue" ink showed very little migration of chloride during the time allotted, while a maximum migration was shown with "Shaeffer's Skrip Permanent Royal Blue."

These results seemed in principle to be at variance with tests made by one of the experts for the prosecution. This man, a chemist for a large ink manufacturer, testified that he had made up a number of inks containing methylene blue or methyl violet dye. To these inks he had added various amounts of hydrochloric acid (presumably forming hydrochlorides of the dyes) and of inorganic chlorides (of unspecified composition). When these inks were used for writing on a sheet of paper, the chemist observed no difference among the various inks in the rate of migration of the chloride away from the ink stroke.

In view of this apparent discrepancy with results of the present authors, and since the case of the young man has not yet been finally adjudicated, it was decided to carry out further tests. Sanford's Royal Blue ink was selected for these tests, since the previous sample had been shown to give a slow chloride migration. Various inorganic compounds were added to samples of this ink, as indicated in Figure 1, to determine whether chloride migration could be accelerated or retarded.

The writing was done December 21, 1937. On January 26, 1938, the right-hand strip was cut off and the chloride metallics were developed as metallic silver. The center strip was cut off March 8, and developed in the same way.

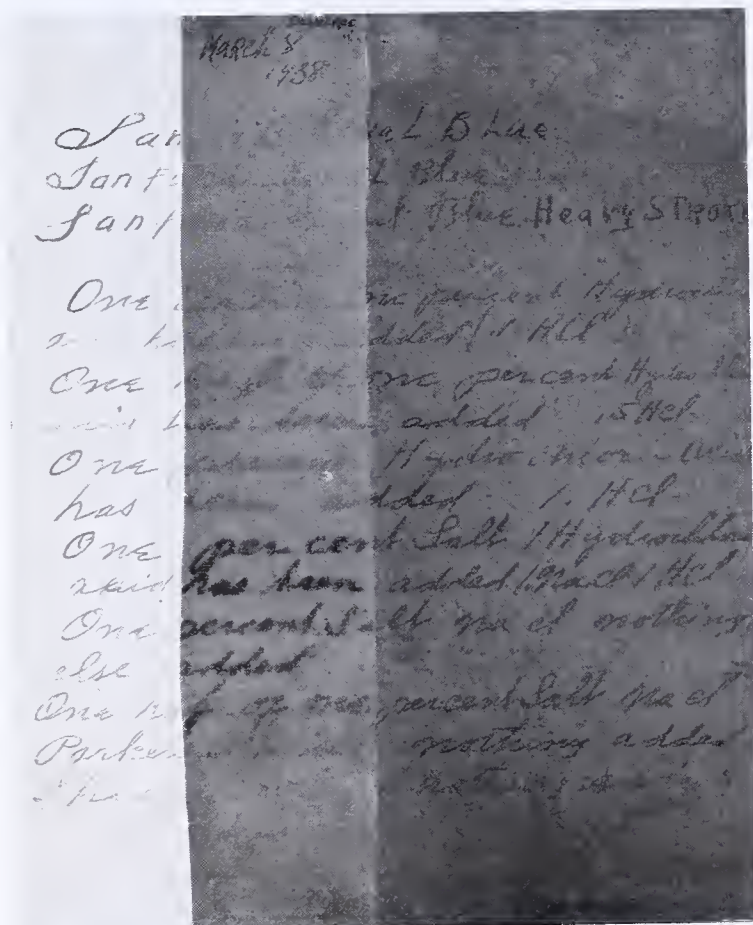


FIGURE 1. CHLORIDE MIGRATION TESTS



It is evident that salt progressively migrates without evaporation. It was found that the rate of chloride migration from the ink strokes was greatly increased by the addition of sodium chloride, and to a lesser extent by hydrochloric acid. The hydrochloric acid image appears, however, to fade rapidly, largely disappearing from the paper.

Some of the results are shown in Figure 1, which speaks for itself. The third line from the bottom was written with an ink containing 0.5 per cent of sodium chloride, or about 0.30 per cent of added chloride. The image is much heavier than that in the eighth and ninth lines from the bottom, where the ink used contained 1 per cent of 12 *N* hydrochloric acid, or about 0.425 per cent of added chloride. It appears, therefore, that in the latter case the chloride must be dissipated by some process other than diffusion through the paper; evaporation of the hydrochloric acid seems the only possible explanation.

### Effect of Added Chloride

Experiments were also made to compare the effects of adding chlorides of sodium, calcium, zinc, copper, and tin. It was thought that the more deliquescent chlorides, such as calcium and zinc chlorides, might show a more rapid chloride migration than sodium chloride. Previous investigations had shown that the rate of chloride migration was very sensitive to moisture content—for example, samples of writing stored a few inches from a steam-heated radiator showed no detectable chloride migration even after six months. But as far as could be observed, the sodium, calcium, zinc, and cupric chlorides, when added to the ink, gave essentially the same rate of chloride migration.

A totally unexpected result was found with stannous chloride, which seemed, when added to ink, to give practically no chloride migration from the ink stroke; the extent of the migration was considerably less than with the untreated ink. The explanation may be as follows: Stannous chloride is

probably rapidly oxidized to stannic compounds on the paper. There are only two added chloride atoms for each tin atom, so that a basic stannic chloride is probably formed. Such a substance may well bind the chloride firmly enough essentially to prevent its diffusion. But on addition of silver nitrate, silver chloride is probably formed, so that a silver image is developed by the chloride test wherever there has been insoluble basic stannic chloride.

An alternative explanation may be that the tin remains as nondiffusible, stannous compounds, which reduce silver nitrate directly and give a spurious "chloride" test. The paper was therefore carefully observed after immersion in the silver nitrate, but before developing. No blackening was seen at this stage, showing that the image from the stannous ink must have been a genuine chloride image; the silver had been first precipitated as silver chloride and not as silver metal. It therefore appears that stannous chloride, added to the ink, definitely slows the rate of migration of the chloride in the paper.

### Conclusion

Since so many factors are concerned in the chloride test for age of inks, any conclusions regarding age of writing, as determined by this test, should be viewed with extreme suspicion.

Inks used by federal offices and in banks should contain a definitely known amount of sodium chloride. This would not only aid in readily identifying the ink, but would also make it possible to determine something of the time element.

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# Evaluation of the Vitamin A Potency of Feeds

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THE most important values of commercial feeds are their productive energy, digestible protein, and bulk or volume. Fraps (4, 7) has shown that the prices of unmixed feeds are, in general, related to their productive energy and digestible protein; with bulky feeds, such as hays, bulk or volume also has a cost. Some feeds have additional values on account of special constituents. These include alfalfa meal and alfalfa-leaf meal on account of vitamin A potency, milk products on account of vitamin G, and bone meal on account of calcium and phosphorus.

The fact that domestic animals under some conditions, do not receive enough vitamin A has recently been recognized. Growing chickens and laying hens are the most frequent sufferers in this respect (26, 27, 28). Milk cows may suffer from vitamin A deficiency when fed on low-grade roughage (5). Other animals may also receive insufficient vitamin A, when fed on restricted rations, as when the pastures have dried up. Even when fed sufficient quantities to maintain good production, hens may not receive enough vitamin A to produce eggs of high vitamin A potency and milk cows may not receive enough to produce milk or butter fat high in vitamin A potency (5, 27, 28).

Recognition of these deficiencies and desire to correct them have led to demands for information regarding the vitamin A potency of feeds, and methods for evaluating suitable carriers of vitamin A potency. Biological methods for estimating vitamin A potency, such as the Sherman-Munsell method, the U. S. P. method, and the single-dose method, are expensive, require considerable time, and are not highly accurate. They are suitable for special purposes but not practical for the commercial evaluation of animal feeds.

### Vitamin A Potency

Vitamin A potency may be due either to vitamin A, a colorless substance, or to carotene or cryptoxanthin, yellow substances. Carotene seems to be changed to vitamin A by animals and stored as such, for the most part in the liver.

Vitamin A as such is not present in animal feeds unless fish liver oils or their concentrates have been added, and when so added may be almost entirely destroyed in 4 weeks (6). The loss of added vitamin A has been studied by Fraps and Kemmerer through absorption of ultraviolet light at 328  $\mu$  as measured in a spectrograph (6). This is not at present a practical method of evaluating the vitamin A



content of feeds. All feeds examined contained substances which absorbed light at the same wave length as vitamin A, 328 m $\mu$ , and are called for convenience pseudo-vitamin A. Corrections for the pseudo-vitamin A may be made by comparing a sample to which no additions have been made with the sample to which the fish liver oil has been added. On account of possible variations of pseudo-vitamin A in different samples of the same feed, this method is not at present suitable for evaluating the vitamin A added to feeds in the form of fish liver oils or their concentrates.

Vitamin A potency of feeds now appears to be derived entirely from carotene (2, 8, 12, 24, 29, 30), with the exception of yellow corn, in which cryptoxanthin, closely related to carotene, is a source of vitamin A potency. Of the three carotenes,  $\alpha$ ,  $\beta$ , and  $\gamma$ , the  $\beta$ -carotene is the most widely distributed (13, 32, 36). According to Kuhn and others, little or no  $\alpha$ -carotene occurs in grasses (15, 17). The bulk of the carotene was found by MacKinney (16) to be  $\beta$ -carotene in 59 plant species. The vitamin A potency of feeds may therefore be evaluated by estimating their carotene and cryptoxanthin content.

### Estimation of Carotene

A method for estimating carotene was presented by Schertz in 1923 (25). Guilbert (11) and the Bureau of Dairy Industry, U. S. Department of Agriculture (18), have proposed methods especially adapted to feeds. Modifications of the Guilbert method have been proposed by Peterson, Hughes, and Freeman (19) and by Fraps and Kemmerer (6, 18). Other methods have been suggested (14, 20, 22, 23, 35). Methods have been proposed for carotene in flour (3). Clausen and McCoord (1) for biological samples use a single distribution between liquid phases to separate the carotenoids. As associate referee on carotene for the Association Official Agricultural Chemists, Munsey is studying the methods for carotene, which are described in detail in his first report (18).

In the Guilbert method, the feed is refluxed with saturated alcoholic potassium hydroxide, cooled, and extracted with ethyl ether. The ether is separated from the alcohol by additions of water, and the aqueous solution is extracted with ether. The ether is distilled off and the carotene and xanthophyll are dissolved in petroleum ether. The xanthophyll is removed by several extractions with ethanol, and the petroleum ether is washed with water, dried with anhydrous sodium sulfate, concentrated, and made up to volume.

In the Peterson-Hughes modification, the ethyl ether is not used but the petroleum ether is added directly to the alcoholic extract. The Dairy Industry method differs from the Guilbert method chiefly in direct extraction of the feed with alcohol and petroleum ether without the use of the potassium hydroxide, and is more tedious. The Hughes modification of the Guilbert method seems most promising at the present time, although some prefer the Fraps-Kemmerer modification (6). The yellow color of the final carotene solution may be read in a colorimeter by comparison against 0.1 or 0.06 per cent potassium bichromate or a dye solution, or in a photoelectric colorimeter, or the density of absorption of light at 450, 470, and 480 m $\mu$  may be read in a spectrophotometer (18). Reading in a colorimeter against bichromate appears to offer a convenient and rapid method for routine tests, especially where more expensive equipment is not available. Reading the solution in a photoelectric colorimeter with suitable filters may possibly offer a method just as rapid and a little more accurate than a visual colorimeter. The spectrophotometer should be more accurate than the colorimeter, especially when other coloring materials are present besides carotene.

The yellow coloring matter extracted and purified by the methods referred to above is not always pure carotene. Shinn *et al.* (29) showed that carotene preparations may contain other coloring matter besides carotene, especially when the solution was prepared from hay and silage of poor quality. Miller (17) found that some carotene may be removed with

the xanthophyll washed out with methanol and some xanthophyll (about 5 per cent) may remain with the carotene. Fraps and Kemmerer found that the excrement of both rats and chickens contains a yellow pigment, not carotene, even though the animals were fed on rations practically free from carotene. These yellow pigments act like carotene in the chemical procedure, but have absorption curves different from that of carotene. The excretion of over 100 per cent of the carotene fed to cows reported by Whitnah *et al.* (34) is probably due to yellow coloring materials not carotene.

Methods of purifying carotene solutions by selective absorption on magnesium oxide, magnesium hydroxide, or other adsorbents may be developed (29, 31, 33). However, according to Gillam *et al.* (9, 10), carotene may be isomerized by chromatographic adsorption on alumina with production of neo- $\alpha$ -carotene.

Measurements of the absorption of light at different wave lengths by the carotene solutions are being undertaken by means of high-power spectroscopes. Using a high-power monochromator, with 4 prisms, it is possible to separate absorption bands of light not separable by less powerful instruments. Hogness *et al.* (17, 37) devised an apparatus which uses a photoelectric cell, and Miller (17) used this instrument in the study of carotenoids. Such an instrument may be used in the estimation of carotene in the presence of other coloring materials. One is being installed at the Bureau of Dairy Industry, U. S. Department of Agriculture at Beltsville, Md. and another has been ordered for the Indiana Experiment Station at Lafayette, Ind. The high cost of the special equipment required will necessarily confine this spectroscopic method to a few laboratories, but its use may provide correction factors for results obtained on corresponding samples by other methods and help to make the estimation of carotene more accurate. The relation between the carotene content and the biological potency of a number of animal and human foods is being ascertained at the Texas Agricultural Experiment Station. Development of methods for determining carotene enable digestion experiments to be conducted, some of the results of which were reported at the Dallas meeting of the AMERICAN CHEMICAL SOCIETY. The possible destruction of carotene by fermentation or conversion of xanthophyll or other coloring matters into substances which resemble carotene, by the acids in the gastric juice or other digestive processes, remain to be explored (21).

The estimation of the color of hay, as in the commercial grading of hay, is to a certain extent an evaluation in terms of carotene. Hay graded No. 3 in color is low in carotene. No. 2 should contain more carotene than No. 3, and No. 1 on an average should be higher in carotene than No. 2 or No. 3. Hay may have the good color of grade No. 1 and yet not be high in carotene, because the chlorophyll is more resistant to change than the carotene. Grading of hay for carotene by color is not an exact method but, until short methods are developed for use in commercial grading, the color of hay is of importance in considering its quality when vitamin A potency is needed.

The importance of a high carotene content in alfalfa-leaves meal and some other feeds has been commercially recognized. Feeds are being purchased on minimum specifications for carotene in localities as widely separated as New York and California, and analyses are being made to see that the carotene content comes up to specifications. The demand for high-carotene feeds will no doubt lead to improvement in the methods of curing and preserving such hays, so as to maintain a high carotene content.

The vitamin A potency of feeds can therefore be evaluated by the estimation of carotene and cryptoxanthin. Methods for estimating carotene are available, and are being studied and improved. Their accuracy at the present time is prob-



ably as great or greater than the biological methods of rat assay.

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## A Greaseless Stopcock

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WHILE investigating the decomposition of a number of hydrocarbons and other organic vapors such as the alkyl amines it was found that even the most expensive greases used on the stopcocks absorbed critical amounts of the gases. To eliminate this hazard a greaseless stopcock was employed.

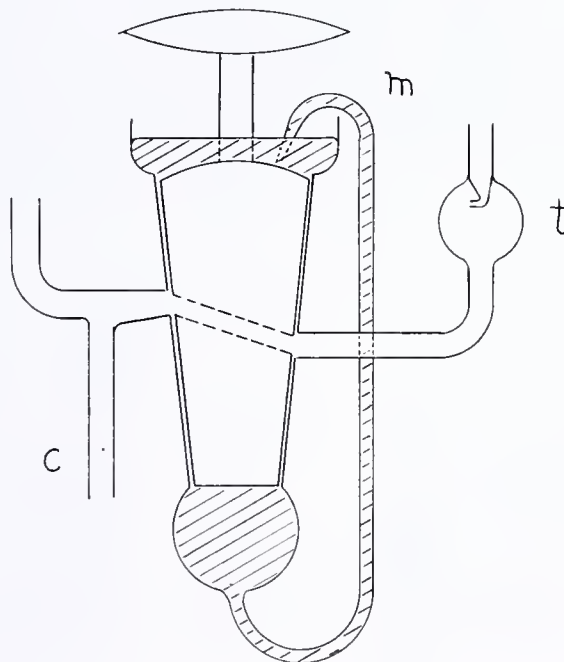
An ordinary mercury-seal stopcock was modified by adding the equilibrating tube, *m*, which allows the system incorporating the stopcock to be evacuated without creating a downward thrust on the plug. With this modification a fine grade of Acheson graphite powder is an excellent lubricant, being ground into the surfaces of the plug and shell until a high black gloss is obtained. This lubricating surface is not completely gastight, but with the mercury seal at top and bottom of the shell the stopcock is perfectly sealed from atmospheric leakage. With a vacuum in the system, and a volume of 100 cc., no leakage was detectable after 3 months' test, pressure being measured with a McLeod gage.

To seal the stopcock against flow through the tubing, a small amount of mercury can be introduced into the tubing by means of tube *c*, which is 1 meter long and stopped by an ordinary stopcock lubricated with graphite placed at the bottom of the tube. A leveling bulb provides the driving force for the mercury.

A small trap, *t*, is placed in the tubing to catch any droplets of mercury which might be entrained in the gas.

The mercury can be very readily directed against the plug and a complete, two-way seal effected. With suitable forethought the stopcock can be operated, like the ordinary greased stopcock, to control flow in both directions. The operator rapidly becomes facile in the use of the device, speed of control approaching that of the ordinary type.

Several of these stopcocks have been used, still with the original lubricant, in the writer's laboratory for a period of 3 years, during which time they have required no care whatever. They are positive in action, insensitive to temperature changes, and completely eliminate the hysteresis effects inherent in the grease-lubricated type.



The use of this stopcock is recommended where it is necessary to eliminate hysteresis effects and the loss of gas volume, such as occurs in the "constant volume" analysis of gases.

RECEIVED July 11, 1938



# Determination of Ethylene Dibromide

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DURING the course of an investigation to determine the identity and amount of the gas, ethylene, given off by some plant tissues during ripening, the present work was undertaken in order to develop a simple method for estimating small amounts of ethylene dibromide. Although it was believed that the reaction of this compound with potassium iodide offered possibilities, inspection of the literature indicated that many substances such as the organic iodides and  $\alpha$ ,  $\beta$ -dibromides, as well as oxidizing and reducing compounds, would interfere in quantitative work.

The reaction of inorganic iodides with  $\alpha$ ,  $\beta$ -dibromides was utilized for analysis of mixtures of normal butenes by Dillon, Young, and Lucas (2), who used the specific reaction rate constants of the dibromo derivatives with potassium iodide in methanol at 75° C. Patterson and Robertson (4) reported the reaction of ethylene bromide with potassium iodide and gave the equation:



Van Duin (3) gave the general equation for all  $\alpha$ ,  $\beta$ -dibromides as:



Dillon (1) showed that the combination of iodine with potassium iodide to form potassium triiodide is probably complete, and thus the reaction may be written in the form:



In any event, the iodine liberated by the reaction as above may be titrated with sodium thiosulfate solutions.

## Experimental

Purified ethylene dibromide, boiling at 130.7° C. at 765 mm., was used to prepare standard solutions in 95 per cent ethyl alcohol. Aliquots of these solutions were employed for the determinations. Preliminary tests indicated that reagent quality potassium iodide refluxed with double-distilled water

and alcohol for 30 to 200 minutes liberated no free iodine. Similarly, 10.00-ml. portions of 0.01 *N* iodine refluxed with water, alcohol, and potassium iodide for 60 minutes gave recovery equal to 10.02 ml. of 0.01 *N* thiosulfate, demonstrating that no loss was caused by reaction of alcohol (or its impurities) with iodine.

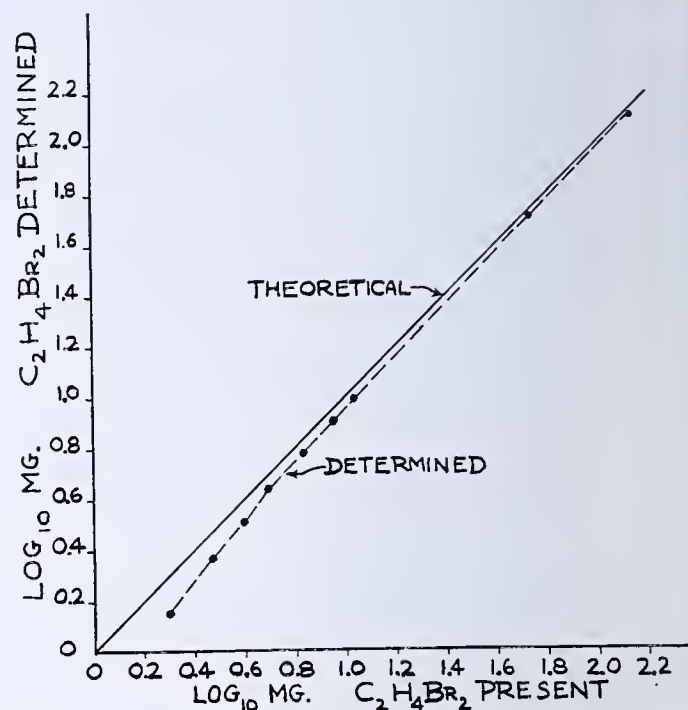


FIGURE 1. DETERMINATION OF ETHYLENE DIBROMIDE

Trials proved that the reaction of ethylene dibromide with potassium and sodium iodide solutions was rather slow. Further, water-iodine-ethylene dibromide mixtures, upon refluxing, lost both iodine and dibromide. Addition of alcohol proved effective in minimizing these losses.

The reaction, according to Dillon (1), is second order. However, in the presence of a large excess of potassium iodide

TABLE I. DETERMINATION OF ETHYLENE DIBROMIDE

Present Mg.	Determined Mg.	Average Mg.	Average Deviation from Mean Mg.	Per Cent Recovery	Present Mg.	Determined Mg.	Average Mg.	Average Deviation from Mean Mg.	Per Cent Recovery
1.000	0.639 0.676	0.658	...	65.8	9.000	8.054 8.124 8.124 8.105	8.102	0.024	90.0
2.000	1.437 1.428	1.433	...	71.7					
3.000	2.386 2.404 2.386 2.339	2.379	0.020	79.3	11.000	9.946 10.01	9.978	...	90.7
4.000	3.287 3.297 3.259 3.250	3.276	0.019	81.9	27.39	25.83 25.83 25.92 25.64	25.81	0.080	94.2
5.000	4.330 4.367 4.395 4.386	4.370	0.021	87.4	54.78	52.60 52.13 52.31 52.69	52.43	0.21	95.7
7.000	6.072 6.138 6.088 6.127	6.106	0.026	87.2	136.95	132.6 133.1 132.4 132.6	132.7	0.23	96.9



it should be pseudomolecular, with the rate of reaction proportional to the first power of the ethylene dibromide concentration. Thus, as the amount of ethylene bromide present is reduced to a few milligrams or less, it is to be expected that the reaction will be slow. Experimentally it was found that it was not practical to extend the reflux period beyond 180 minutes and that a variation of 10 minutes in this period introduced no significant error.

### Procedure

The preliminary work led to the adoption of the following standard technic:

Ten milliliters of 20 to 30 per cent potassium iodide solution and 50 ml. of alcohol are placed in a 250-ml. flask and the sample to be analyzed is added. The flask is then fitted to a water-cooled condenser by a ground joint and the liquid is heated sufficiently to maintain a gentle reflux for 180 minutes. At the end of this period the source of heat is removed, the flask and contents are allowed to cool to room temperature, and the condenser tube is rinsed with a few 10-ml. portions of water.

The liberated iodine is then titrated with 0.01 or 0.1 *N* sodium thiosulfate. Sufficient water is added to the flask to bring the total volume to approximately 200 ml., to minimize the effect of the alcohol upon the starch-iodine end point.

### Results and Discussion

The results are given in Table I and are illustrated graphically in Figure 1.

Inspection of the data shows that the average deviation from the mean over the whole range of ethylene bromide concentration is less than 1 per cent of the determined value. However, it is apparent that this method, particularly for amounts of ethylene bromide below 25 mg., may not be used without error unless a correction is applied. It is believed that the precision and reproducibility are of sufficiently high order to justify the use of the method when a calibration or correction curve is plotted.

### Summary

A simple method proposed for the quantitative determination of ethylene dibromide involves reaction of the sample with potassium iodide and titration of the liberated iodine. The method does not give complete recovery, and many substances interfere. However, it is capable of giving reproducible results, and in the absence of interference these determined values may be corrected by use of a correction curve.

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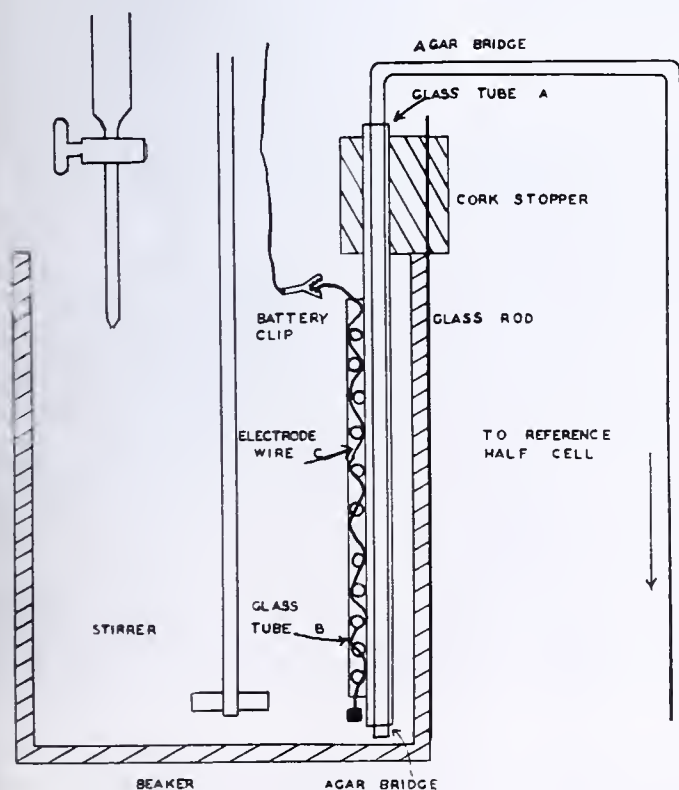
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RECEIVED April 30, 1938.

## Simple Electrode Support for Electrometric Titrations

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THE simple device shown in the sketch has proved very useful for electrometric titrations. Glass tube *B* has several small holes in it to prevent unstirred solution from collecting within. This tube is held to tube *A* by rubber bands. The electrode wire, *C*, is a thin wire, made of the same metal as the electrode. This system has the following advantages:

The electrode can be easily removed and cleaned by ignition in a flame. This cannot be readily accomplished using the ordinary glass seal-mercury connection, since heating may produce small cracks in the glass which, as shown by Morgan, Lammert, and Campbell (*1*), can materially alter the potential obtained.

The electrode and agar bridge are held close to the edge of the beaker, preventing contact with the stirrer.

The electrode and agar bridge are held close together, diminishing the resistance in the circuit. This is of especial importance when working with solutions of low conductivity.

The device can be easily prepared in a few minutes' time from simple material, available in any laboratory. It can be very easily attached to or removed from the beaker, without the use of clamps or other supports.

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RECEIVED May 4, 1938. Published with the permission of the Commissioner, U. S. Bureau of Fisheries.



# The Determination of Organic Halogen

## A Simplified Lime Ignition Method

R. H. KIMBALL AND LEWIS E. TUFTS

Hooker Electrochemical Company, Niagara Falls, N. Y.

The sample is weighed in a gelatin capsule and ignited in a Pyrex tube filled with hydrated lime. Combustion takes place in a short tube furnace, the contents are dissolved in nitric acid, and the solution is titrated directly for chloride or bromide without filtration.

OVER a hundred years ago von Liebig analyzed organic substances by destruction with quicklime and gravimetric determination of the calcium halide (3). The procedure was improved and used extensively by Delbridge (2), who combined it with the Volhard titration and recommended it for especially firmly bound chlorine. By taking advantage of the striking improvement in the Volhard technic recently introduced by Caldwell and Moyer (1), this historic method becomes really rapid and convenient. It involves only simple equipment, can be handled by the average laboratory assistant, and has been used in this laboratory for more than five hundred determinations with complete success.

### Materials

The combustion is carried out in 15 × 300 mm. Pyrex tubes, closed at one end and flared at the other (Will Corporation, Rochester, N. Y.). The sample is weighed in a gelatin capsule (standard capsules, size No. 00, Parr Instrument Co., Moline, Ill.). Powdered hydrated lime nearly or entirely chlorine-free is used (Chemical Lime Co., Bellefonte, Pa.). Ignition takes place in an ordinary 20-cm. (8-inch) tube furnace with rheostat control (such as the multiple unit, type 70-S, Hevi-Duty Electric Co., Milwaukee, Wis.).

### Procedure

Five centimeters (2 inches) of lime are put into the combustion tube, and the capsule containing the sample (0.2 to 0.8 gram) is uncovered and dropped in. Volatile substances are introduced in a closed capsule, with a pinhole in the cover to allow slow distillation as the temperature rises. The tube is then filled to within 5 cm. (2 inches) of the top with lime, making no attempt to mix the sample with the lime. Viscous liquids are preferably handled by dropping the uncovered capsule into the empty tube, flowing the contents over the lower portion, and then filling the tube with lime.

The charged tube is held in a horizontal position and rapped sharply to open up a generous passage the full length above the lime, in order to permit the escape of moisture and other gases. It is laid in the furnace (which may already be hot) so that only the front of the lime is heated, and the end containing the sample projects out and is screened by a circle of asbestos paper. When the sample is volatile, a current of air is directed on the exposed end of the tube and prevents distillation before the lime is hot; in this way even carbon tetrachloride can be successfully burned. After the front of the lime is red hot, the tube is rotated and moved forward gradually in the furnace, until the sample is completely burned and the end containing it is brought to a full red heat. This takes from 45 minutes to an hour, when the tube is removed from the furnace and allowed to cool.

To facilitate removal of the contents, a piece of stiff Monel wire longer than the tube and bent back sharply to form a handle is pushed down through the tube contents to the bottom. Tube and wire are then inverted in a 500-ml. glass-stoppered Erlenmeyer flask containing 70 to 100 ml. of distilled water, and

by sliding the irregular wire up and down the tube the contents are easily brought down into the water (Figure 1). The outside of the tube and the projecting wire are rinsed with hot 3 *N* nitric acid, the tube is turned upright, and the wire is washed down into the tube and lifted out. The tube is rinsed with the hot nitric acid until any remaining lime has been dissolved and all halide washed out, when it is discarded. Solution of the lime is completed by the addition of concentrated nitric acid, which also oxidizes the trace of sulfide resulting from the gelatin capsule, and the solution is ready for titration.

When the substance analyzed contains sulfur it is necessary to remove remaining sulfide at this point by adding a strong solution of ceric sulfate (about 0.5 *N* in 2.5 *N* sulfuric acid) until the yellow color persists. The excess is removed before titration with a few drops of hydrogen peroxide.

The solution, which sometimes contains much free carbon, is titrated quickly and easily without filtration by the Volhard method as modified by Caldwell and Moyer (1). The addition of nitrobenzene, which they recommend to coagulate and stabilize the silver chloride, serves equally well to clarify the solution and yield a sharp end point. The best procedure is the following:

If the solution is not warm, it should be reheated. Standard 0.1 *N* silver nitrate is added in an excess of 5 to 15 ml. over the amount required. Ten milliliters of a half-saturated solution of ferric ammonium sulfate (prepared by dissolving 2.268 kg., 5 pounds, of ferric ammonium alum in 2 liters of water containing 30 ml. of concentrated sulfuric acid, and adding 3 liters more of water) are added, and a few (measured) drops of standard 0.1

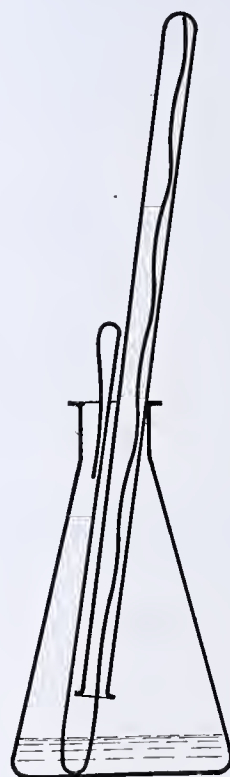


FIGURE 1

*N* ammonium thiocyanate to confirm the presence of excess silver nitrate. Back-titration with the thiocyanate is then continued to within a few milliliters of the end point. Ten milliliters of nitrobenzene (Eastman Kodak Co. practical) are added and the flask is stoppered and shaken vigorously. All suspended matter collects in the globule of nitrobenzene, leaving the solution clear; if an unusual amount of carbon is present, another 10 ml. of nitrobenzene may be added. Back-titration is continued to a good pink color persisting for 5 minutes. A few milliliters of silver nitrate are then added and back-titrated to a second end point, which should check the first within 0.05 ml. or better. (The same treatment can be applied to other solutions containing suspended material. For example, sulfide is readily titrated by allowing a measured sample to flow down a funnel underneath the surface of excess standard silver nitrate solution slightly acidified with acetic acid. A few milliliters of dilute nitric acid are then added and the solution is back-titrated as described without filtration of the silver sulfide precipitate.)

If the lime contains chloride, a blank should be run on each bottle by duplicating the determination without the sample. The volume of silver nitrate used is subtracted from that required by the sample, and from the corrected volume the per cent of halogen is calculated.

From six to nine determinations can be made in a day with a single furnace. Although no iodo compounds have been



TABLE I. ANALYTICAL RESULTS

Compound	Theory %	Found %	Difference %	Compound	Theory %	Found %	Difference %
Carbon tetrachloride	92.20	91.92	-0.28	p-Chloronitrobenzene	22.52	22.56	+0.04
		92.12	-0.08			22.27	-0.25
		91.97	-0.23				
Chlorobenzene	31.52	31.52	0	Methyl α-phenyl-β-bromo-β-benzoylpropionate	23.03	23.03	0
		31.67	+0.15			23.10	+0.07
p-Dichlorobenzene	48.26	48.21	-0.05	Methyl α,γ-diphenyl-α, β-dihydroxy-γ-chlorobutyrate	11.06	11.03	-0.03
		48.20	-0.06			10.83	-0.23
Tetrachlorobenzene	65.70	65.64	-0.06	2,3,4,6-Tetrachlorophenylbenzoate	42.34	42.39	+0.05
		65.45	-0.25			42.41	+0.07
p-Chloroacetanilide	20.91	20.89	-0.02	Hexachlorobenzene	74.72	74.98 <sup>a</sup>	+0.26
		20.82	-0.09			74.85 <sup>a</sup>	+0.13
p-Bromoacetanilide	37.34	37.31	-0.03			75.02 <sup>a</sup>	+0.30
		37.49	+0.15			74.83 <sup>a</sup>	+0.11

<sup>a</sup> Lime contained 15 per cent calcium nitrate.

analyzed in this laboratory, the lime ignition method is known to be applicable to them, with some special precautions (3). Experiments are now in progress to test the usefulness of the method on a semimicro scale.

The analytical results in Table I represent the usual accuracy of the method. The reputation of hexachlorobenzene as one of the very few substances not completely decomposed by lime ignition (3) was confirmed when the usual procedure gave results as much as 2 per cent below the theory. The difficulty is easily overcome by mixing 15 per cent of powdered

anhydrous calcium nitrate with the lime, and the figures shown in Table I were obtained in this way.

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RECEIVED June 21, 1938.

# Improved Method of Heat Input Control in Glass Fractionating Columns

G. H. MOREY, Commercial Solvents Corp., Terre Haute, Ind.

THE kettles of all-glass analytical columns are usually heated by an oil bath or, electrically, by resistance wires which are immersed in the liquid and sealed through the walls of the flask. This is usually satisfactory for small quantities of material which are fractionated for analytical purposes only. Occasionally it is necessary to use an all-glass column for preparing large amounts of pure compounds for use in other work. If the kettles are glass flasks of 5-liter capacity or over, heating by means of an oil bath is undesirable because such a large quantity of hot oil constitutes a fire hazard, accurate heat input is difficult, and if the column floods it is

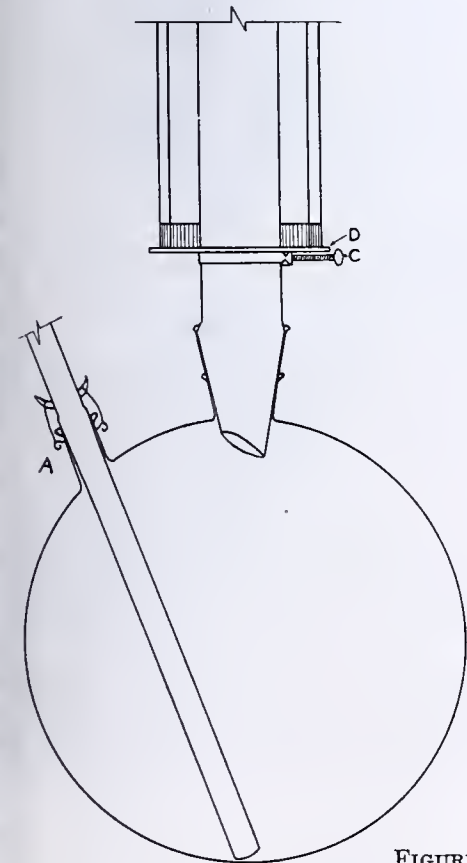


FIGURE 1. KETTLE

difficult to remove the source of heat from the kettle quickly. Heating large volumes of liquid (of the order of 10 liters) by electrical immersion heaters is impracticable for several reasons, chief among which is the desirability of heating the flask over its entire surface in order to prevent undue condensation of the vapors before they can enter the column.

The method of heating described herein was designed to overcome these difficulties.

Apparatus

The column proper was of Pyrex glass, 3.12 cm. (1.25 inches) in inside diameter and 150 cm. (5 feet) long, and was packed with the single-turn glass spirals developed at the Pennsylvania State College. The heating jacket for the column was a Pyrex tube 55 mm. in inside diameter and 150 cm. (5 feet) long, wound with Nichrome wire in two sections of 500 watts each. The outer jacket was a Pyrex tube 71 mm. in diameter and 150 cm. (5 feet) long. The construction of the column followed conventional designs.

The kettle (Figure 1) was a 12-liter flask fitted at the top with the female part of a 40/50 ground-glass joint which was attached to the bottom of the column. A 24/40 ground-glass joint was sealed into the flask about 7.5 cm. (3 inches) from the top, for the purpose explained below. A mantle of thin asbestos cloth was sewed about the flask with asbestos thread. Then another mantle of heavy asbestos cloth was sewed over the first. Patterns were first cut from ordinary cloth to determine the size and the best method of cutting to avoid wrinkles. The mantles before sewing on to the flask looked like Figure 2. In the second mantle, Nichrome wire was sewed spirally around the flask from the bottom up. The distance between each turn was about 0.94 to 1.25 cm. (0.375 to 0.5 inch). In this way three circuits of 500 watts each were sewed around the flask: one at the bottom, one around the middle, and one around the top side. Each circuit was controlled by a Variac.

The first mantle prevented the hot wires from touching the flask at any point. The heating wire was then insulated against excessive radiation losses by winding asbestos rope around the



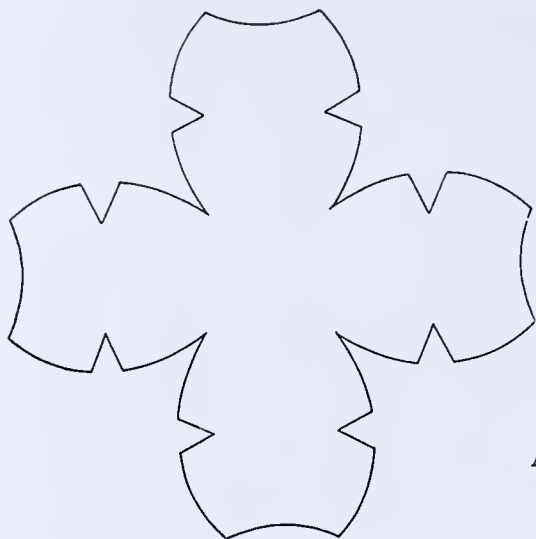


FIGURE 2.  
ASBESTOS MANTLE

flask from the bottom up. Each turn of rope was held against the flask by pieces of asbestos thread tied into the mantle at one or two points. Another mantle of asbestos cloth was then sewed over the outside. The terminals of the heating units were silver-soldered to copper strips  $1.25 \times 5$  cm. ( $0.5 \times 2$  inches). These heating units were then connected to the source of current by battery clips which were insulated from one another by drawing short pieces of rubber tubing over them. With this arrangement, the kettle could be quickly disconnected for cleaning.

In order to hold the kettle against the ground-glass joint at the bottom of the column, a cradle of wire netting shaped like a half sphere was made. The lower half of the kettle rested in this cradle and springs suspended from a circular iron standard were connected to the cradle. The tension of the springs held the kettle and contents against the bottom of the column. An iron ring clamped around the top of the kettle prevented too much pressure against the ground-glass joint as the flask became empty. The springs were of the type used on screen doors and were 1.25 cm. (0.5 inch) in diameter by 12.5 cm. (5 inches) long. Twelve of these springs were used. No trouble during several months of operation has been experienced because of freezing of the ground-glass joint. The smaller ground-glass joint sealed into the flask about 7.5 cm. (3 inches) from the large ground-glass joint was provided for filling the kettle and to permit observations within the kettle during operation.

A 5-volt flashlight bulb, the lead wires of which were enclosed in a copper sheath, could be lowered into the long glass tube at A (Figure 1) extending to the bottom of the kettle. Looking down through the top of the kettle, it was possible to see when the bulb dipped below the surface of the liquid. A scale on the copper sheath then indicated the number of liters still left in the kettle.

In order to prevent the column from being pushed up through the heating jacket as the flask became empty, a flat aluminum disk, D, was placed at the bottom of the jackets. Beneath this disk some asbestos tape was wound around the column and over this a clamp, C, was tightened. This clamp was of the type used to tighten hose connections in automobile radiators. The complete assembly of the kettle is shown in Figure 3.

### Discussion

This method of heating the kettle permits of very accurate heat input control. Once the Variacs are set at the desired points, the column will operate for hours with no attention during the time that one constituent is being fractionated out. It is desirable to wind a 12-liter flask in three circuits so that, as

the liquid level becomes lower, the current in the upper circuits can be diminished, preventing superheating of the vapors. The major portion of the heat can then be furnished where it is needed most—viz., at the bottom circuit where the heat for boiling the liquid is absorbed. This effect can be accomplished in one circuit for flasks of 1-liter capacity by allowing a greater distance between turns of the Nichrome wire toward the top of the flask.

The asbestos cloth and sewing cord used in the construction may be purchased from the Johns-Manville Corporation. The grades of cloth are designated as follows: No. 1067 asbestos cloth, 0.08 cm. (0.03 inch) thick, No. ME3010 asbestos cloth, and No. 285 asbestos cord, 0.16 cm. (0.062 inch) thick.

The Variacs are purchasable from the General Radio Company, Cambridge, Mass.

It is well to have the joints sealed to the larger flasks at glass-working shops which are equipped for thorough annealing of such large pieces.

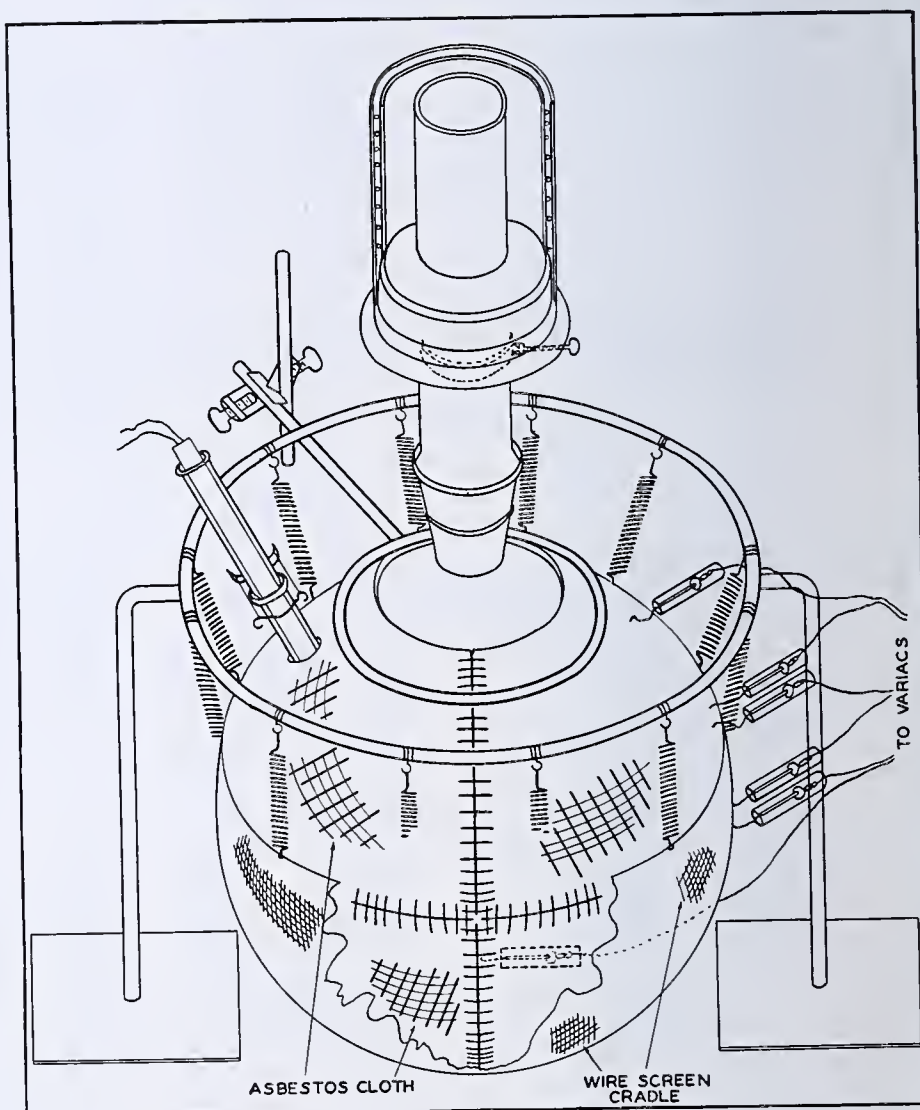


FIGURE 3. COMPLETE KETTLE ASSEMBLY

Woven glass fabrics would probably serve much better than asbestos cloth. It is possible that the seams of such fabrics could be fused together with a blow torch instead of by sewing.

Since round-bottomed flasks are made up to 22-liter capacity, it is possible to construct all-glass columns of nearly semicommercial proportions using kettles heated in this manner.



# Determination of Small Amounts of Nicotine on Apples

## And Adaptation of the Official Method to Apple Foliage

WILLIAM RALSTON, Tobacco By-Products and Chemical Corporation, Richmond, Va.

A method for determining the small quantities of nicotine found on sprayed apples is presented. The novelty of the method consists essentially in washing nicotine from the fruit with a mixture of aqueous sodium hydroxide solution and ethylene dichloride, from which the nico-

tine is recovered. The nicotine is then distilled and precipitated with silicotungstic acid. The results are accurate to 0.1 mg. over the range 0 to 12 mg. of nicotine on a 1-kg. sample. The method applies to both water-soluble and water-insoluble nicotine insecticides.

THE distillation procedure in the official method of analysis for nicotine (1) cannot be used in determining the spray deposit on apples because the sample should be at least 1 kg., and removal of the nicotine from this bulk by distillation is impractical. Using only the peelings from the apples does not help because charring inevitably results. To obviate these difficulties the nicotine is washed from the fruit by dilute sodium hydroxide and ethylene dichloride. The sodium hydroxide frees the nicotine from any salts present, since no salt of nicotine is stable in alkaline solutions and the dichloride dissolves enough of the wax coating of the apples to assure complete residue removal.

with 25 to 35 ml. of water and the washings are placed in the second separatory funnel. One milliliter of concentrated hydrochloric acid is added and the whole is shaken vigorously. On separation the solvent layer is drained off and the acid layer is added to the first acid treatment in the Kjeldahl. About 50 to 75 ml. are boiled off to expel any solvent present. On cooling, 20 ml. of sodium hydroxide (sp. gr. 1.35) are added and the nicotine is distilled into a 400-ml. beaker containing 10 ml. of hydrochloric acid (1 to 4).

The distillation consists of boiling the nicotine down almost to dryness and then passing a current of steam through it until a volume of about 300 ml. is collected. The volume of liquid in the Kjeldahl should be kept as small as possible.

The precipitation of the nicotine in the distillate follows, as given in the official method. The precipitate is filtered and washed four times with hydrochloric acid (1 to 1000). The Gooch crucible and precipitate are ignited at 900° C. for 10 minutes.

TABLE I. RECOVERY OF NICOTINE

No. of Apples	Weight of Apples <i>Grams</i>	Nicotine Added		Nicotine Recovered <i>Mg.</i>	Percentage Recovery
		<i>Ml.</i>	<i>Mg.</i>		
Nicotine sulfate with 1% corn (Karo) sirup, 1 ml. = 0.56 mg. of nicotine					
10	990	0	0	0	
8	900	1.0	0.56	0.45	80.4
12	1160	4.6	2.57	2.58	100.0
10	1060	10.0	5.60	5.51	98.3
10	1240	10.0	5.60	5.54	99.0
10	1160	10.0	5.60	5.56	99.3
10	1192	10.0	5.60	5.56	99.3
10	1301	20.0	11.20	11.18	99.8
Nicotine bentonite, 1 ml. of suspension = 0.62 mg. of nicotine					
10	1216	20.0	12.40	12.43	100
10	1305	20.0	12.40	12.36	100

### Experimental

Gooch crucibles were adopted because of speed in filtration and ease of washing. Four washings were found to be sufficient. Trouble was experienced in getting consistent weighings. It was found that cooling the crucibles to room temperature on an Alberene slab gave more accurate weighings than using a desiccator in the usual way.

The recovery of nicotine from apples by the proposed method was tested, with the results shown in Table I. The insecticides chosen for this purpose were (1) nicotine sulfate with 1 per cent corn (Karo) sirup and (2) nicotine bentonite. The former represents a class of water-soluble nicotine products, while the latter is largely water-insoluble. From other work it was found that nicotine is lost from these products very slowly, with practically no loss in 10 days from open Petri dishes.

The apples were placed in the receptacle used for washing and a measured amount of the solution or suspension was pipetted in, in such manner that the stem and calyx cavities would receive some. After standing until dry, usually 24 to 36 hours, the determinations were made.

These results show a recovery high enough to warrant proposal of the method.

### Determination of Nicotine on Apple Foliage

The usual method of steam distillation may be employed to determine nicotine on foliage. A sample consisting of 50 leaf disks 3.81 cm. in diameter is taken. About 800 ml. are distilled over and acidified with 15 ml. of hydrochloric acid (1 to 4). By precipitating from this large volume and siphoning off most of the supernatant liquor, the usual tedious

Dilute hydrochloric acid is used to extract the nicotine from the solvent. The acid washing is then made alkaline and the nicotine is distilled as outlined in the official method. Gooch crucibles with pads made of long-fiber ignited and acid-washed asbestos are used because of ease and rapidity in filtration.

### Procedure

A tin can 13 × 13 × 26 cm. with wide mouth and friction top is used for washing the fruit. A nail hole in one of the top corners will allow complete drainage. According to size of fruit and residue expected, 8 to 12 apples are weighed and placed in the can and 175 ml. of ethylene dichloride and 25 ml. of 1 per cent sodium hydroxide solution are added. The top is put on tightly and the whole is thoroughly shaken for 1 minute. The liquor is drained from the fruit into a 500-ml. separatory funnel. The fruit is washed again exactly as described and then given a final rinse with about 40 ml. of ethylene dichloride. All washings are collected in the separatory funnel. Five milliliters of concentrated hydrochloric acid are added and the whole is shaken thoroughly.

After separation the bottom or solvent layer is drawn off into another 500-ml. separatory funnel and the top or acid layer is run into a Kjeldahl flask. The first separatory funnel is rinsed



TABLE II. RECOVERY OF NICOTINE FROM APPLE FOLIAGE

[Sample consisted of 50 leaf disks, 3.81 cm. in diameter, to which was added the indicated amount of nicotine. One milliliter of nicotine solution (nicotine sulfate with 1 per cent corn, Karo, sirup) = 0.56 mg. of nicotine.]

Nicotine Added		Nicotine Recovered	
Ml.	Mg.	Mg.	%
0	0	0	99
10.0	5.60	5.54	100
20.0	11.20	11.23	100
20.0	11.20	11.16	100

evaporation to about 100 ml. can be avoided. Table II shows some results obtained by this procedure.

Whenever it is necessary to keep foliage for some time before analysis, the sample should be placed in a jar with 50 ml. of hydrochloric acid solution (1 to 9). In this way samples have been kept for 10 weeks with no loss in nicotine.

## Summary

A method for determining the small quantities of nicotine found on sprayed apples is presented. Its novelty consists essentially in washing nicotine from the fruit with a mixture of aqueous sodium hydroxide solution and ethylene dichloride, from which the nicotine is recovered, then distilled, and precipitated with silicotungstic acid. The results are accurate to 0.1 mg. over the range 0 to 12 mg. of nicotine on a 1-kg. sample. The method applies to both water-soluble and water-insoluble nicotine insecticides.

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RECEIVED April 22, 1937.

# A Simplified and Portable McLeod Gage

EARL W. FLOSDORF, University of Pennsylvania, Philadelphia, Pa.

VARIOUS modifications of the McLeod (3) gage have been proposed; perhaps the most common uses a low degree of vacuum on the atmospheric side to allow the mercury to be withdrawn from the bulb (1). To cause the mercury either to enter or leave the bulb, the present gage utilizes a metal swivel (2) that bears all the weight of the gage. A reading may be made in 2 to 3 seconds; the gage is compact, uses a minimal quantity of mercury, and is portable. Sudden changes of pressure do not affect the gage, whether it is under vacuum or not.

In Figure 1 the gage is shown diagrammatically in position *R* for reading, and (in broken lines) when turned to position *P* for acquiring the pressure of the system to be measured. For pressures above 0.001 mm., in order that the gage may be turned on swivel *S*, heavy-walled rubber tubing free from sulfur and talc is satisfactory for connection to the vacuum system at point *A*. For lower pressures a ground joint is

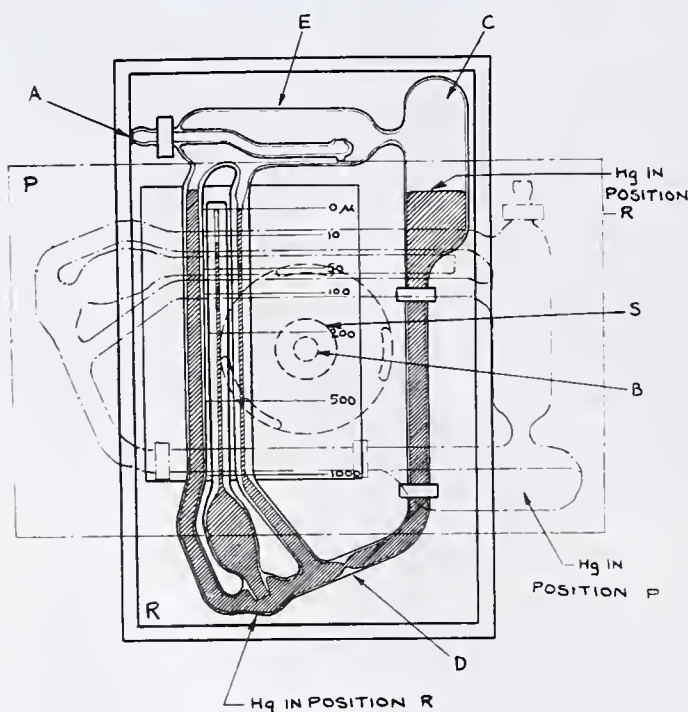


FIGURE 1. SIMPLIFIED MCLEOD GAGE  
Front view showing two positions

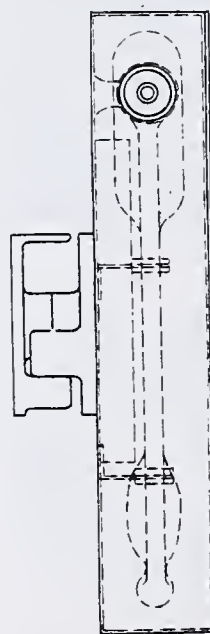


FIGURE 2. SIMPLIFIED GAGE  
Side view showing swivel, case, etc.

used to permit turning the gage on the swivel, and glass tubing is brought from point *A* to point *B*, where it is passed out through the back of the metal case. The vacuum connection is attached at *B*, in the center of the swivel axis, by a glass-to-metal ground joint, so that all rubber connections are avoided. With either device, the gage may be turned very rapidly in making a reading with no danger of breaking and may also be easily disconnected and rendered portable. Figure 2 is a side view, showing details of the swivel.

In position *P*, which is not exactly horizontal, the mercury will drain completely into bulb *C*. A constriction at point *D* prevents the mercury from traveling too rapidly into and out of the capillaries, so that the gage may be swung very rapidly to and from position *R*. The diameter of bulb *C* is such that when a pressure reading is made, the mercury in the right-hand capillary always comes to the top line, irrespective of whether or not the mercury is high or low in the center capillary. The safety trap, *E*, permits the portable gage to be carried while full of mercury without loss of mercury even when inverted.

## Acknowledgment

The author wishes to acknowledge the helpful assistance of J. D. Graham, the University of Pennsylvania glass blower, in the construction of these gages. Gages of several ranges may be obtained through the F. J. Stokes Machine Company, Olney, Philadelphia, Pa.

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RECEIVED July 11, 1938.



# Spectrographic Examination of Assay Beads for Platinum, Palladium, and Gold

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THIS research was undertaken to develop a qualitative spectrographic procedure which would reduce the time necessary for determining platinum, palladium, and gold in ores.

De Laszlo (3) has described a method for estimating platinum in silver assay beads by counting the number of platinum spark lines. The authors have had little success with this method for the determination of platinum and palladium in assay beads. However, detection of the precious metals by their spark lines has the advantage of leaving the bead intact for subsequent wet analysis.

The second spectrographic procedure developed consists in qualitatively detecting minute traces of the metals by examination of their arc lines. Particular attention has been paid to the possible interference of the lines of platinum, palladium, gold, rhodium, iridium, and ruthenium; these, with silver and lead, are the only metals likely to be present in a silver assay bead.

Gold beads containing platinum and palladium, comparable to the annealed residues from sulfuric acid partings of silver assay beads, were also treated by the arc method.

## Preparation of Electrodes

In the preparation of silver beads containing the precious metals, lead containers were made from spectrographically pure lead foil. To each box, solutions of the precious metals were added from microburets. The solutions were carefully evaporated on hot plates, then the boxes were rolled up with a weighed amount of silver foil, wrapped in more lead foil, and compressed under a pressure of about 100 kg. per sq. cm. The resulting 30-gram cylinders were cupeled at 900° C. and the beads left in the muffle

for 2 minutes after "the blick" to remove most of the lead. The weights of silver and precious metals reported are, in all cases, the weights added to the lead boxes.

A standard gold chloride solution, containing 0.25 mg. of gold per cc., was prepared from spectrographically pure metal and analyzed by the method of Beamish, Russell, and Seath (2). Palladium and platinum chloride solutions, each containing 0.25 mg. of the metal per cc., were prepared from the spectroscopically pure metals. Standard iridium, rhodium, and ruthenium solutions, also containing 0.25 mg. of the metal per cc., were made by fusion of the metal sponges with sodium peroxide in a silver crucible as suggested by Beamish and Russell (1). Silver was removed as the chloride. Further dilution of these solutions made possible the use of microburets for adding traces of the precious metals to the lead boxes.

In both the arc and the spark treatments the beads were part of the lower electrode. Spectrographically pure gold, palladium, platinum, and silver wires of 3-mm. diameter were used in the production of the comparison spectra, and the other electrodes employed were purchased from Adam Hilger, Ltd., London, England.

## Spark Analysis

In the production of bead spark spectra the secondary of the transformer delivered 10,000 volts, 60 cycles per second. The spark gap was kept constant at 3 mm. and the light from the spark was focused on the slit of a Hilger medium quartz spectrograph, E<sub>3</sub>, by means of a spherical condensing lens with a focal length of 17 cm.

Supersensitive H. and D. No. 650 Zenith plates were used with the developer and fixer prescribed by the manufacturer. The time of development was 2 minutes; fixation and washing required 30 minutes each. The dried plates were studied over

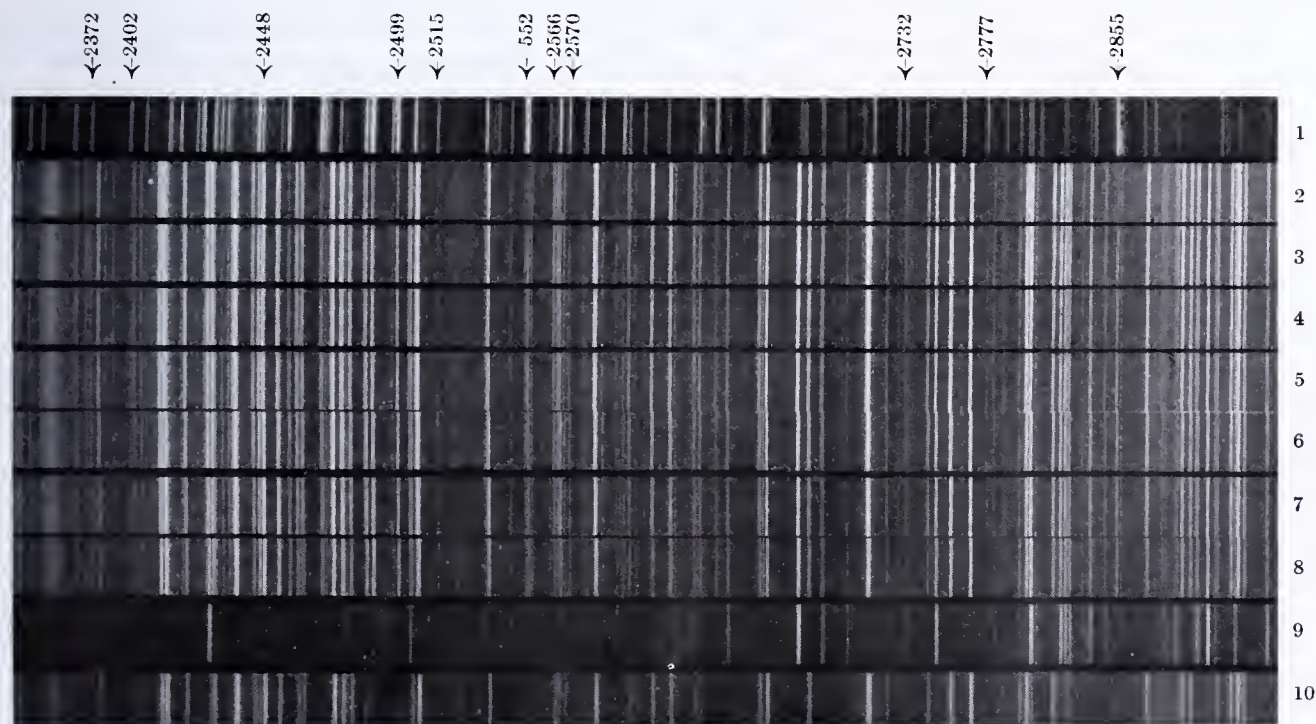


FIGURE 1. SPARK SPECTRA OF 50-MG. SILVER-PALLADIUM BEADS WITH GOLD AS THE UPPER ELECTRODE

1. Palladium spark spectrum
- 2-8. Spectra of gold and bead containing: (2) 2.0 per cent of palladium; (3) 2.5 per cent of palladium; (4) 3.0 per cent of palladium; (5) 3.5 per cent of palladium; (6) 4.0 per cent of palladium; (7) 4.5 per cent of palladium; (8) 5.0 per cent of palladium
9. Gold spark spectrum
10. Silver spark spectrum



an aperture in a closed box with interior lighting, by means of a magnifying glass.

The wave lengths for the lines reported are given in International Angstrom units (4, 6). The spectral region studied was between 4000 Å, and 2000 Å.

Fifty-milligram silver-platinum and silver-palladium beads were investigated by the spark method. In order to photograph a series of beads rapidly, a simple container was designed, consisting of a small silver cup made of silver foil, inserted in one end of a glass tube of 3-mm. diameter and attached beneath to a silver wire threaded through the 6-cm. tube and connected to the lower terminal of the spark stand. The beads were easily removed from this holder after sparking. As only a small part of the bead was vaporized it was difficult to conclude what weight of the precious metal the spark would detect. Table I records the lines consistently obtained for the lowest concentrations when a silver wire was the upper electrode. Figure 1 represents spectra of silver-palladium beads in which the upper electrode was a gold wire.

TABLE I. SPARK SPECTRA

Wave Length Å.	Lowest Concentration Observed %	Wave Length Å.	Lowest Concentration Observed %
Platinum Lines, Silver-Platinum Beads			
3204.1	0.08	2702.4	0.02
3064.7	0.01	2659.4	0.20
3042.6	0.04	2650.9	0.08
2998.0	0.02	2646.9	0.02
2893.9	0.04	2572.7	0.80
2830.3	0.04	2515.7	0.80
2794.2	0.02	2514.0	0.80
2771.7	0.04	2467.4	0.20
2733.9	0.40	2450.9	0.40
2719.0	0.08	2442.7	0.80
2705.9	0.04	....	..
Palladium Lines, Silver-Palladium Beads			
3894.2	0.08	3481.2	0.20
3799.2	0.60	3460.8	0.30
3718.9	0.20	3433.4	0.30
3690.4	0.08	3421.2	0.20
3634.7	0.02	3404.6	0.02
3609.5	0.02	3373.0	0.20
3571.2	0.20	3242.7	0.20
3553.1	0.30	3114.6	0.60
3517.0	0.08	3065.3	0.20
3489.8	0.60	....	..

The sensitivity of this method is much greater than that of the method of surface effects, the inadequacies of which have been pointed out by Forbes and Beamish (5).

Arc Analysis

In the production of bead arc spectra the current was 2 amperes, the arc gap about 3 mm., and the voltage approximately 40 volts. Since the method did not require the exact reproduction of electrical conditions, slight variations were not detrimental. In all other respects the photography of the arc was similar to that of the spark, except that arc exposures were 2 minutes.

Silver, gold, bismuth, zinc, and tin were not satisfactory as electrodes because they melted at the arc temperature. Copper, nickel, and molybdenum introduced too many interfering lines. Soft carbon electrodes burned too rapidly and made it impossible to keep the bead on the lower electrode for more than a few seconds. Graphite electrodes of 6.3-mm. diameter were found satisfactory since they burned slowly, did not melt at the arc temperature, and produced very few interfering lines in the composite spectrum. The deficiency of silver arc lines also assisted in the detection of the precious metals as their lines were not masked.

The upper graphite electrode was sharpened after each exposure and the lower one was rounded off, leaving a small

nick for the bead. Before putting the bead in place the arc was struck for a few seconds to remove surface contamination. In every case the lower electrode was made the anode, since the beads decomposed rapidly and the blackening of the carbon bands was reduced. After 2 minutes' arcing 50- and 100-mg. silver beads and 10-mg. gold beads were only partly decomposed but 10-mg. silver beads were almost completely decomposed.

TABLE II. ARC SPECTRA

Wave Length Å.	Lowest Concentration Observed %	Wave Length Å.	Lowest Concentration Observed %
Platinum Lines, Silver-Platinum Beads			
3064.7	0.004	2733.9	0.008
3042.6	0.004	2705.9	0.04
2998.0	0.004	2702.4	0.04
2830.3	0.008	* 2659.4	0.04
Palladium Lines, Silver-Palladium Beads			
3894.2	0.006	3460.8	0.004
3718.9	0.03	3433.4	0.004
3690.4	0.006	3421.2	0.001
3634.7	0.001	3404.6	0.001
3609.6	0.02	3302.1	0.006
3571.2	0.006	3242.7	0.001
3553.1	0.02	3114.1	0.004
3517.0	0.006	3027.9	0.006
3489.8	0.03	2763.1	0.004
3481.2	0.004	....	...

The lines tabulated in Tables II and III were consistently found to be present in the spectra of beads made up to contain the recorded percentages.

Binary Systems

SILVER-PLATINUM. A series of 10-mg. silver-platinum beads was arced and the platinum lines for the lowest concentrations are recorded in Table II. Thus as little as 0.0004 mg. of platinum can be detected in a 10-mg. silver bead and there are no interfering lines. This is more sensitive than the stannous chloride spot test. The most persistent lines for platinum were found to be 3064.7, 3042.6, 2998.0, 2830.3, and 2733.9.

SILVER-PALLADIUM. The most persistent palladium lines observed in the spectra of a series of 10-mg. silver-palladium beads are also tabulated in Table II. The arc will detect at least 0.0001 mg. of palladium in a 10-mg. silver bead, which is as sensitive as the dimethylaminobenzilidine rhodanine spot test. Silver and graphite lines did not interfere. The most persistent lines were 3634.7, 3421.2, 3404.6, and 3242.7.

SILVER-GOLD. Ten-milligram silver-gold beads were arced and the gold lines for the lowest concentrations are recorded in Table III. The arc will detect at least 0.0001 mg. of gold in a 10-mg. silver bead. Figure 2 represents a typical series of silver-gold beads, the two most persistent lines being 2428.0 and 2676.0.

TABLE III. ARC SPECTRA

Wave Length Å.	Lowest Concentration Observed %	Wave Length Å.	Lowest Concentration Observed %
Gold Lines, Silver-Gold Assay Beads			
3122.8	0.04	2688.7	0.80
3029.2	0.40	2676.0	0.001
2748.3	0.02	2641.5	0.40
2700.9	0.08	2428.0	0.001
Platinum Lines, Gold-Platinum Beads			
3064.7	0.006	2733.9	0.03
3042.6	0.006	2705.9	0.04
2998.0	0.006	2702.4	0.05
2830.3	0.03	2659.4	0.05
Palladium Lines, Gold-Palladium Beads			
3894.2	0.03	3460.8	0.01
3718.9	0.04	3433.4	0.01
3690.4	0.02	3421.2	0.006
3634.7	0.006	3404.6	0.006
3609.6	0.04	3302.1	0.02
3571.2	0.02	3242.7	0.006
3553.1	0.04	3114.1	0.01
3517.0	0.02	3027.9	0.02
3489.8	0.05	2763.1	0.03
3481.2	0.01	....	...



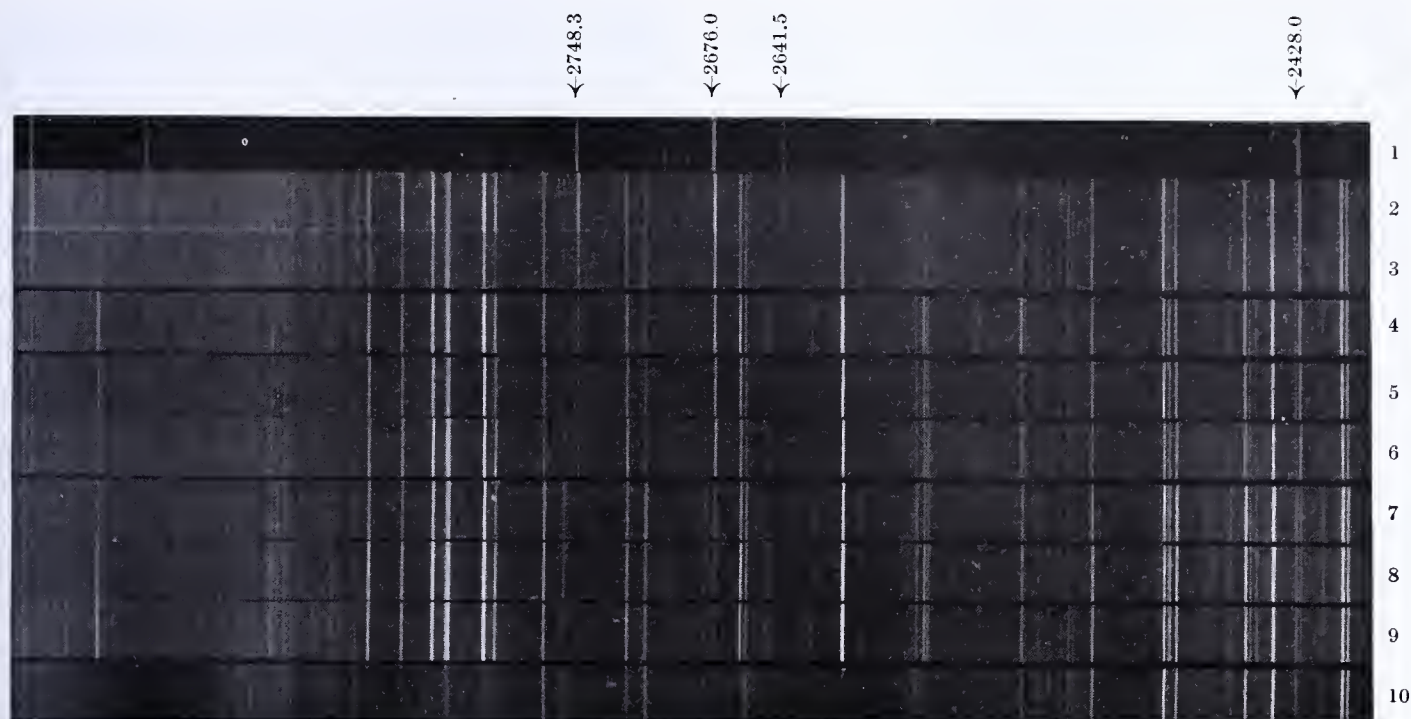


FIGURE 2. ARC SPECTRA OF 10-MG. SILVER-GOLD BEADS

1. Gold arc spectrum
- 2-9. Spectra of silver bead containing: (2) 0.75 mg. of gold; (3) 0.25 mg. of gold; (4) 0.12 mg. of gold; (5) 0.08 mg. of gold; (6) 0.04 mg. of gold; (7) 0.008 mg. of gold; (8) 0.004 mg. of gold; (9) 0.002 mg. of gold
10. Arc spectrum of silver and graphite

**GOLD-PLATINUM.** The most persistent platinum lines observed in spectra of 10-mg. gold-platinum beads are also recorded in Table III. After 2 minutes' arcing, at least half of the bead was intact; so the method will detect at least 0.0006 mg. of platinum in a 10-mg. gold bead.

**GOLD-PALLADIUM.** Ten-milligram gold-palladium beads were arced and the palladium lines are recorded in Table III. The arc method detects at least 0.0006 mg. of palladium in a 10-mg. gold bead.

### Polycomponent Systems

Silver and gold beads containing two or more of the precious metals in small quantities were arced to determine the sensitivity of the method for platinum, palladium, and gold in polycomponent beads and to investigate interference of the precious-metal lines.

Ten-milligram silver beads containing equal amounts of platinum and palladium were arced and only platinum line 3064.7 and palladium line 3065.3 produced interference. At least 0.0004 mg. of both platinum and palladium can be detected in a 10-mg. silver bead.

Similarly, it was found that platinum and palladium did not interfere with gold lines in spectra of 10-mg. silver beads, containing equal weights of the precious metals. At least 0.0001 mg. of gold could be detected in the 10-mg. composite bead.

Ten-milligram silver beads containing equal proportions of platinum, palladium, gold, and iridium were arced. Iridium interfered with certain platinum lines, especially with line 3064.7, when more than 0.05 mg. of iridium was present in a 10-mg. composite bead. Otherwise there was no interference.

Ten-milligram silver beads containing equal amounts of platinum, palladium, gold, and rhodium were similarly arced and no rhodium lines were found to interfere.

Ten-milligram silver beads containing equal weights of platinum, palladium, gold, and ruthenium were arced in the same way. Ruthenium lines did not interfere when less than 0.05 mg. of the metal was present in a 10-mg. silver bead.

Ten-milligram gold beads containing equal proportions of platinum and palladium were arced and at least 0.0006 mg. of each metal could be detected with no line interference.

As the proportion of platinum, palladium, and gold usually greatly exceeds that of the other associated platinum metals

in the common sources, the interference caused by iridium, rhodium, and ruthenium can generally be ignored.

### Summary

The authors suggest the preparation of duplicate assay beads for preliminary spectrographic examination which may modify the subsequent wet analysis for the precious metals. If lines of palladium, platinum, and gold are not present in the bead spectrum, the tedious time-consuming separations of these metals may be avoided.

Silver-platinum and silver-palladium beads can be sparked for the detection of traces of platinum and palladium.

Minute traces of platinum, palladium, and gold are more accurately detected by arcing silver assay beads than by spot tests.

Traces of platinum and palladium can be detected in gold beads comparable to the annealed residues from sulfuric acid partings of silver assay beads.

When the proportions of iridium, rhodium, and ruthenium are low in the bead, there are very few interfering arc lines in the composite bead spectra.

### Acknowledgment

The authors are indebted to H. J. C. Ireton of the Department of Physics, University of Toronto, for invaluable assistance.

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# Sulfur Determinations from Bomb-Washings Titrations

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IN THE Parr procedure for B. t. u. determinations (1), carried out in an Emerson or Parr oxygen bomb calorimeter or similar apparatus, the total heat which is the product of the temperature rise from the combustion of a sample and the water equivalent of the calorimeter is too high. The proper value is obtained by applying the wire correction, the acid correction, and the sulfur correction. These are collectively termed the total correction.

The wire correction is the heat given off by the fuse wire that is burned when it ignites the fuel in the bomb. The fuse wire is so drawn that 1 cm. when burned will give off 2.8 calories of heat; 2.8 times the length of wire burned is the wire correction.

The acid correction is due to the heat of formation of the nitric acid formed in the combustion. When neutralized with sodium carbonate solution (1 ml. equals 1 calorie), the number of milliliters required for a bomb-washings titration is the acid correction. However, some of the acid neutralized is sulfuric acid, whose heat of conversion from sulfur dioxide to sulfur trioxide is greater than the heat of formation of an equivalent amount of nitric acid. The heat of conversion is the difference between the heat of formation of sulfur dioxide, which is formed in ordinary combustion, and the heat of formation of sulfur trioxide, which is formed in the bomb. The difference between the heat of conversion of sulfur dioxide to sulfur trioxide and the heat of formation of an equivalent amount of nitric acid amounts to 1300 calories per gram of sulfur. Then  $13 \times$  per cent of sulfur  $\times$  weight of fuel sample equals the sulfur correction.

Obviously, a B. t. u. determination of most fuels requires a sulfur determination. The gravimetric method used in the routine B. t. u. determinations referred to below is briefly: Precipitate the sulfuric acid in the bomb washings by excess barium chloride solution, allow to stand, filter, ignite, and weigh the residue as barium sulfate. Duplicate determinations can easily be checked within 5 in the second decimal place of the percentage of sulfur—i. e., 1.30% — 1.35%. This is also its approximate accuracy. This accuracy is more than is necessary for a B. t. u. determination, but it is useful in determining a very desirable correlation between the percentage of sulfur and the bomb-washings titration.

## Correlations

The sulfur percentages and average milliliters of bomb-washings titrations from the routine B. t. u. determinations of 54 oils were plotted and by the method of least squares the most suitable straight line was determined (Figure 1). The expression found was:  $M - 11.46 = 6.36 S$ .

Since the assumption was that the amount of nitric acid formed is a constant, the question is raised: How much is this constant affected by the amount of nitrogen in the fuel and also by the heat of combustion of the oil? Figure 2

shows the variation of the calculated total corrections from the standard total corrections (where sulfur is actually determined), plotted against the nitrogen percentage of the fuel. The oil nitrogen was determined by the Kjeldahl method, and, although of uncertain accuracy, Figure 2 shows that the correction appears reasonably constant up to 1 per cent of nitrogen. Figure 3 shows the variation of the calculated corrections from the standard total corrections plotted against B. t. u. per pound of the oil. The variation was not affected between 18,000 and 19,000 B. t. u. per pound. These two figures show that the nitric acid constant was not affected appreciably within the prescribed limits, about 1 per cent of fuel nitrogen and B. t. u. per pound range from 18,000 to 19,000 (10,000 to 10,556 calories per gram).

## Application

In the above the coefficient of correlation was 0.92, showing good agreement. Figure 3 shows that in about 96 per cent of the cases plotted the total correction calculated from the developed equation had an adverse effect of only 6 B. t. u.'s. The accuracy of the correlation can also be seen from the comparison of the calculated slope with the theoretical slope.

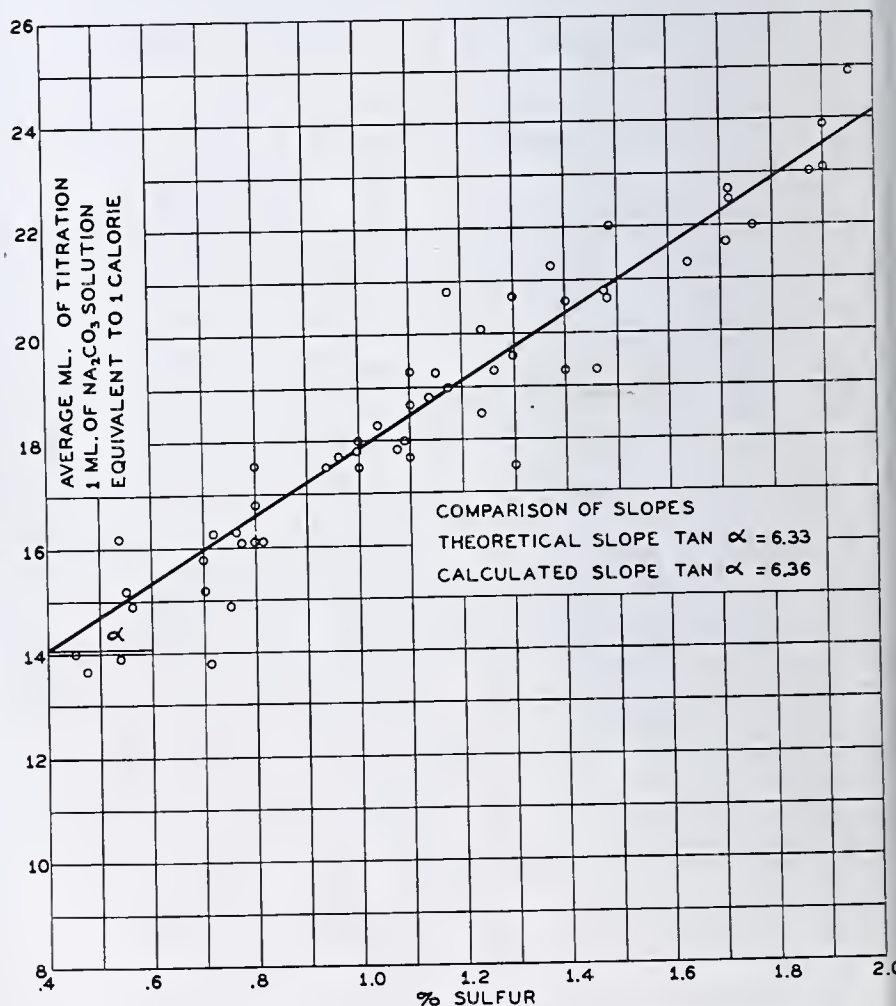


FIGURE 1. SCATTER OF POINTS ABOUT CALCULATED CURVE



Calculated slope  $\tan \alpha = 6.36$   
Theoretical slope  $\tan \alpha = 6.33$

CALCULATION OF THEORETICAL SLOPE. The equation for relating the milliliters of bomb-washings titration and the percentage of sulfur in a 0.7-gram sample of oil is:

$$M - a = mS$$

where  $M$  = ml. of titration  
 $a$  = nitric acid constant  
 $m$  = slope of  $\alpha$   
 $S$  = percentage of sulfur in a 0.7-gram sample

The chemical reaction between sodium carbonate and sulfuric acid is  $\text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{H}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ . Since the weight of sulfur is proportional to the weight of sodium carbonate with which it reacts, the following proportion readily obtains:

$$\frac{S}{\text{Na}_2\text{CO}_3} = \frac{\text{weight of sulfur}}{\text{weight of Na}_2\text{CO}_3}$$

If the weight of sodium carbonate is 0.003658 gram (the weight of sodium carbonate in 1 ml. of solution used in titrating bomb washings), the corresponding weight of sulfur is 0.0011064 gram. Then 0.007 gram of sulfur (weight of sulfur in a 0.7-gram sample, 1 per cent sulfur) divided by 0.0011064 gives the milliliters of sodium carbonate solution equivalent to 1 per cent of sulfur.

$$\frac{6.326}{0.0011064/0.007000}$$

Then

$$\frac{M - a}{S} = 6.33$$

All calculations given thus far are based on a 0.7-gram sample of fuel, the actual size of sample burned. However,

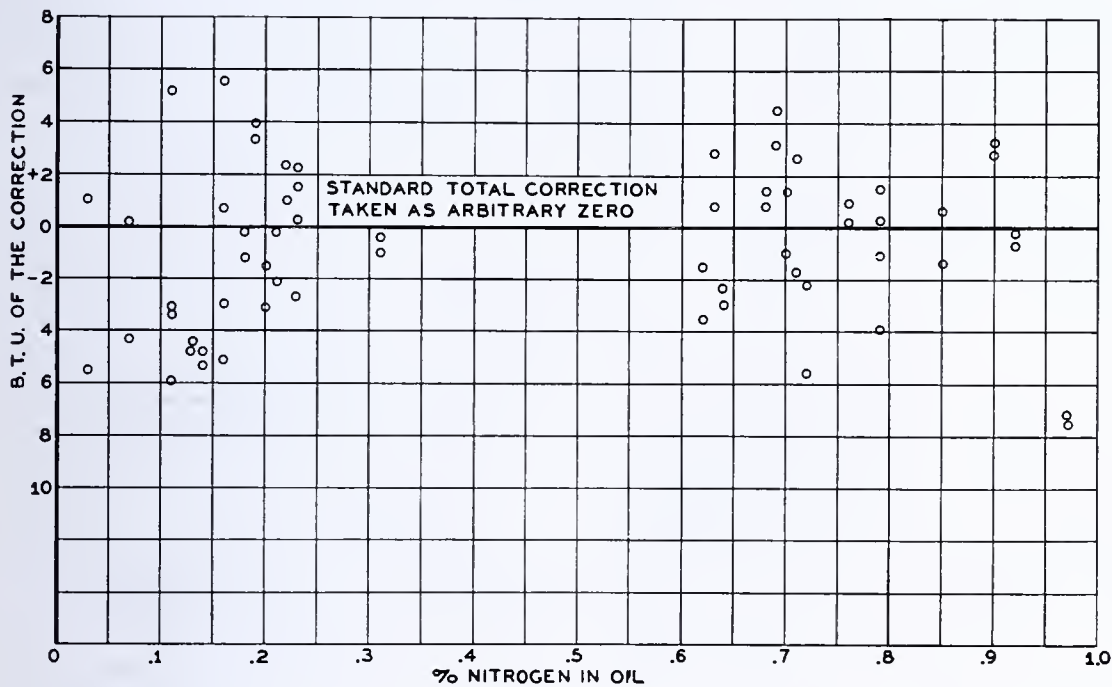


FIGURE 2. VARIATION OF CALCULATED TOTAL CORRECTIONS FROM STANDARD TOTAL CORRECTIONS AGAINST NITROGEN PERCENTAGE OF OIL

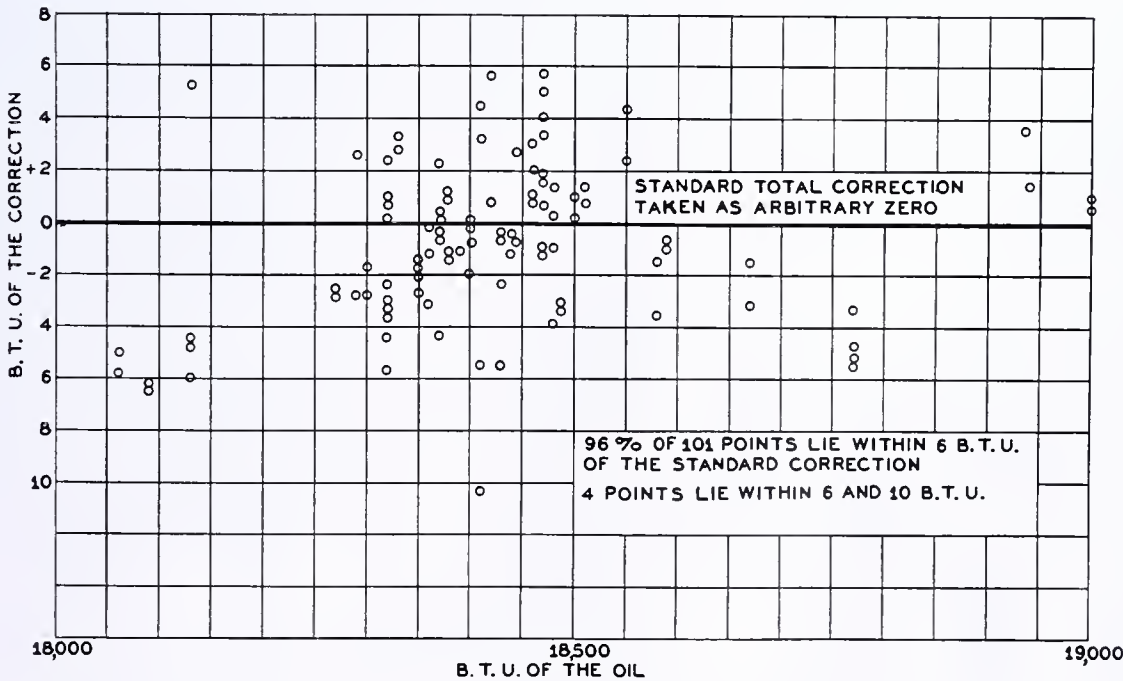


FIGURE 3. VARIATION OF CALCULATED TOTAL CORRECTIONS FROM STANDARD TOTAL CORRECTIONS AGAINST B. T. U.'S OF OIL



if the B. t. u. correction only is required, it is much simpler to avoid the intermediate steps involving sulfur percentages or weight, and to convert the sulfur correction directly to calories and combine with the corrections due to acid and wire.

Original equation

$$M - 11.46 = 6.36 S \quad (1)$$

Since  $S$  is in per cent

$$\frac{S \times 0.7}{100} = G \quad (2)$$

$G$  = grams of sulfur

Substituting 2 in 1

$$M - 11.46 = \frac{6.36}{0.007} G \quad (3)$$

Since sulfur correction is 1300 calories per gram

$$1300 \times G = C_1 \quad (4)$$

$C_1$  = calories due to sulfur

Substituting 4 in 3

$$M - 11.46 = \frac{6.36}{9.10} C_1 \quad (5)$$

Transposing

$$\frac{9.10}{6.36} (M - 11.46) = C_1 \quad (6)$$

Simplifying

$$1.431 M - 16.4 = C_1 \quad (7)$$

The expression for acid correction is

$$M = C_2 \quad (8)$$

$C_2$  = calories due to acid

The expression for the wire correction is

$$2.8 L = C_3 \quad (9)$$

$C_3$  = calories due to wire

The expression for the total correction is then

$$C_1 + C_2 + C_3 = C$$

$C$  = total correction

$$C = 1.431 M - 16.4 + M + 2.8 L \quad (10)$$

Simplifying

$$C_1 + C_2 + C_3 = 2.431 M + 2.8 L - 16.4 \quad (11)$$

The expression found is

$$2.431 M + 2.8 L - 16.4 = C$$

Figure 4 shows a series of curves constructed from the above expression for various values of  $L$ .

DEVELOPMENT OF GENERAL EQUATION. For application in another calorimeter setup, since the calculated slope was so close to the theoretical slope, the theoretical slope can be used to develop a general expression for total corrections.

General equation for sulfur percentage and milliliters of titration relation

$$M - a = 6.33 S \quad (12)$$

$$\frac{0.7S}{100} = G$$

$$M - a = \frac{6.33}{0.007} G \quad (13)$$

$$1300 G = C_1$$

$$M - a = \frac{6.33}{9.10} C_1 \quad (14)$$

Transposing and simplifying

$$1.438 M - 1.438 a = C_1 \quad (15)$$

Total correction is

$$C_1 + C_2 + C_3 = C$$

$$C = 1.438 M - 1.438 a + M + 2.8 L \quad (16)$$

Simplifying

$$C = 2.438 M + 2.8 L - 1.438 a \quad (17)$$

To find  $a$ , run a number of sulfur determinations and substitute milliliters of titration (1 ml. contains 0.003658 gram of sodium carbonate) and grams of sulfur in Equation 13. Take an average of at least one dozen determinations.

### Conclusion

From the foregoing it is concluded that the general expression for total correction

$$2.438 \times M + 2.8 \times L - 1.438 \times a = C$$

has application in any calorimeter setup where the fuel nitrogen and B. t. u. content are within limits that have no appreciable effect on the variation of nitric acid formed, where the sulfur percentage is not too high to be substantially converted to sulfuric acid, and where the same oxygen pressure is used for every determination.

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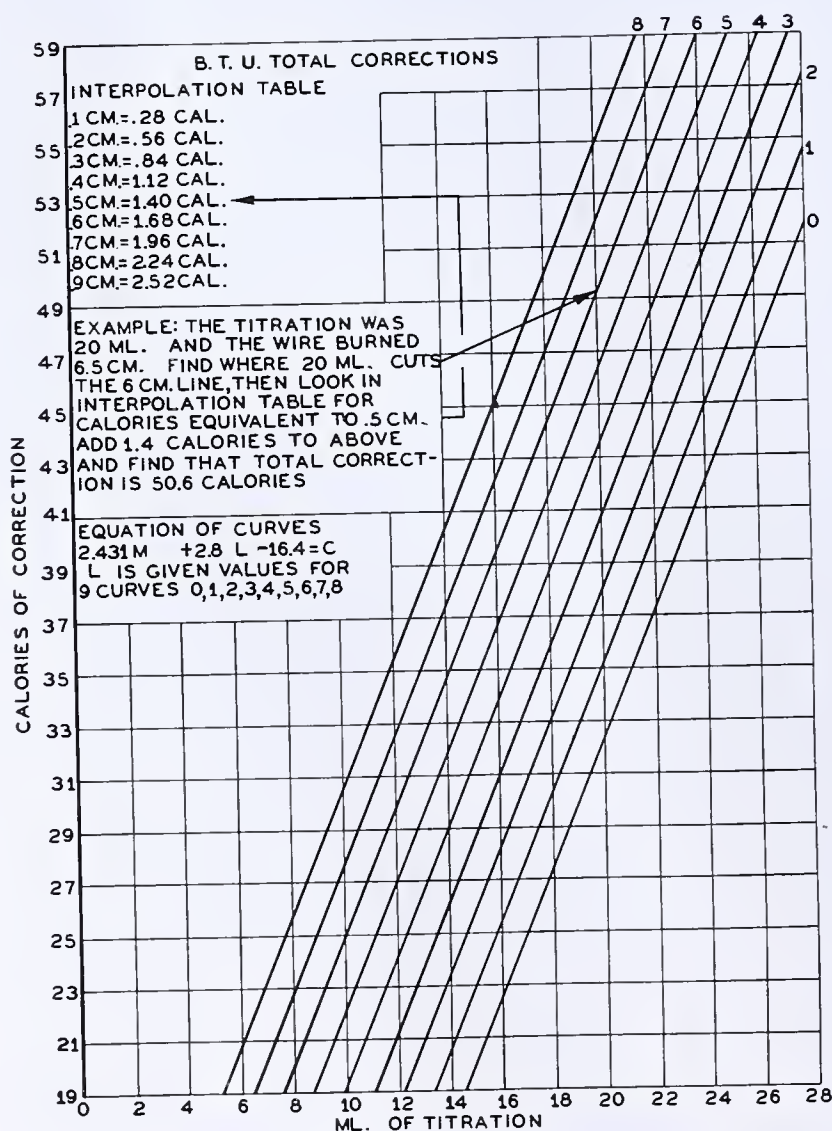


FIGURE 4. CURVES FOR TOTAL CORRECTIONS



# Determination of Alcohol in Pharmaceutical Liquids

## Use of the Chain Hydrometer and Alcohol-Water Temperature Charts

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THE chain hydrometer in its present form was invented and developed by C. W. Foulk, of Ohio State University, and described by him in 1923 (3). The instrument will give accurate density readings through four decimal places in ordinary industrial use and through six places in careful scientific work. Its theory, operation, and construction have been admirably described and illustrated by Foulk (3). Other details are available (1, 4, 5, 7), and there is also an interesting paper by Koch and Smith (6).

Up to the present time the chain hydrometer has been specifically applied to the standardization of hydrochloric acid for analytical use (5, 7) and the estimation of dissolved solids in boiler water (1). As far as the author has been able to ascertain, the chain hydrometer, until now, has never been applied to the measurement of the specific gravity of the alcoholic distillate in a pharmaceutical alcohol determination. A pycnometer is usually employed for this purpose; in fact, the United States Pharmacopœia X specified the use of a pycnometer (9), but this requirement was omitted from the United States Pharmacopœia XI (11). Because pycnometer determinations are time-consuming a new instrument that is both accurate and rapid is desirable. The chain hydrometer is such an instrument.

### Description and Use of Hydrometers

Since the distillate obtained in the usual methods of alcohol determination is clear and colorless, no difficulty is encountered in measuring its specific gravity directly by the chain hydrometer. The methods in common use in this country furnish a distillate of 50 cc., and therefore hydrometers were designed to take that volume of sample and to cover a specific gravity range (referred to water in air at 15.56°) from 1.0000 to 0.9399 or, in terms of equivalent alcohol percentages by volume, from 0 to 47 per cent at 15.56° C.

In the percentage range desired, a difference in density of 0.0001 is equivalent to about 0.06 per cent of alcohol. For routine industrial work, alcohol percentages need not be defined closer than 0.2 per cent—in fact, it is probable that unless extreme precautions are taken the United States Pharmacopœia XI method will not yield consistent results nearer the truth than 0.5 per cent. Numerous interfering substances present in most pharmaceutical preparations will usually make the error greater than this figure. The position of a chain hydrometer bulb in a clear liquid can easily be read directly to one division and estimated to one-half division against a graduated scale in which the divisions are 0.75 mm. apart. Therefore chain hydrometers were desired in which a specific gravity difference of 0.00015 would cause a change of approximately 0.375 mm. in the position of the bulb. It was found that two instruments were necessary to cover the required specific gravity range, in order to keep the tube length short enough to fit in the ordinary 50-cc. graduated cylinder which held the sample.

A jeweler's gold-plated chain which was strong, fairly light

in weight (0.044 gram per cm.), and easily available was chosen for the work. The formula given by Foulk and Brooks (3) concerning the movement of the bulb in a chain hydrometer is

$$\Delta d = \frac{(D - d) \times b \times w}{2D \times V}$$

where  $\Delta d$  = density change in liquid which causes a vertical displacement of float of  $b$  measured in cm.

$D$  = density of material of chain (about 10.7 with most gold-plated chains)

$d$  = density of liquid

$V$  = volume of float measured in cc.

$w$  = weight in grams of 1 cm. of chain

Substituting the above data in this formula,  $V$  was found to be about 5 cc. This volume made the bulb fit conveniently in the graduated tube of the chain hydrometers designed for this work.

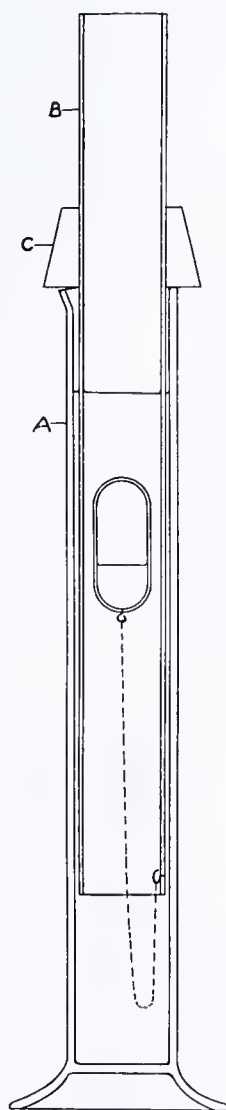


FIGURE 1. HYDROMETER

In Figure 1,  $A$  is an ordinary 50-cc. graduated cylinder, or better, a cylinder that has not been graduated.  $B$  is a graduated tube, 20 cm. long and 1.8 cm. in inside diameter, bearing 130 marks 0.75 mm. apart.  $C$  is a rubber stopper. The bulb is ballasted with carbon tetrachloride, the meniscus of which serves as a reference mark for determining positions on the graduations of tube  $B$ . The gold chain is fastened to the graduated tube and to the bulb with platinum wire, which is sealed into the glass. The length of the chain and the amount of carbon tetrachloride ballast in the bulb are carefully adjusted, so that with one hydrometer the reading is about 100 in water and 0 in 25 per cent alcohol at approximately 25° C., and with the other about 100 in 21 per cent alcohol and 0 in 44 per cent alcohol. The overlapping between the ranges of the two hydrometers is desirable for obvious reasons.

The hydrometers were calibrated with water and water-alcohol mixtures of various strengths. The specific gravities of these mixtures were determined with a pycnometer. The hydrometer readings, temperatures, and specific gravity data were correlated to obtain calibration values for the hydrometers at various points along their graduations. All intermediate graduation marks were determined by interpolation.

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## Alcohol-Water Temperature Charts

Tables published in the United States Pharmacopœia X and XI (10, 12) and based upon work done by the National Bureau of Standards (8) can be correlated and the results plotted to give the accompanying charts (Figures 2 and 3). Larger charts, which can be read directly to 0.1 per cent of alcohol, can easily be made by plotting the data given in the United States Pharmacopœia X (10). The charts are used as follows:

A pycnometer is calibrated with water at 15.56° C. An alcohol-water mixture is weighed at room temperature and its weight is divided by the weight of water obtained in the calibration of the pycnometer. The resulting specific gravity is found on the ordinate of the chart and the horizontal line is followed until the curved line corresponding to the temperature of the alcohol-water mixture is intersected. The abscissa at this point indicates the alcohol percentage by volume at the standard temperature, 15.56° C.

After a chain hydrometer is calibrated, the calibration figures can be put on the chart in place of the specific gravity figures. Then any hydrometer reading at any temperature can be converted to alcohol percentage at the official temperature without calculation. Similarly, the weights of a pycnometer containing various alcohol-water mixtures can be put on the chart in place of the specific gravity figures and the same elimination of calculations results as long as the weight and capacity of that particular pycnometer do not change. The

alcoholic distillate does not have to be brought to any definite temperature in taking its specific gravity when one of these alcohol-water temperature charts is used; this fact, together with the elimination of calculations, results in a marked saving of time over the usual method of alcohol determination.

## Procedure

Distill the sample in the usual way, following the method in the United States Pharmacopœia XI. When interfering volatile substances are present, the method using heptane and a special alcohol receiver (2) is recommended. Bring the clear alcoholic distillate to a volume of 50 cc. with distilled water and transfer it to a dry 50-cc. cylinder. Mix it thoroughly by inverting and righting the cylinder several times (this is important). Allow air bubbles to rise to the top, insert the chain hydrometer, and let the bulb reach equilibrium. When it has come to rest, read its position in the graduated tube and take the temperature of the liquid to the nearest 0.3° C. (The temperature can be conveniently taken by allowing a small thermometer to hang in the graduated tube just above the bulb while the bulb is reaching equilibrium.) Then, by reference to the calibration data or to an alcohol-water temperature chart upon which the hydrometer calibration data have been recorded, the correct alcohol percentage at the official temperature can be obtained.

## Advantages of the Hydrometer

The chain hydrometer offers many advantages over other methods of measuring specific gravities in alcohol determinations. It consumes little manipulative time; placing the hydrometer in the liquid and taking the reading are operations which can be done in seconds, not minutes. This factor is decidedly in its favor when the instrument is compared with the pycnometer or the Westphal balance. When the alcohol-water temperature charts described above are used in connection with the chain hydrometer, results are obtained more rapidly than by any other method.

The ordinary Westphal balance does not give as consistently accurate results as the chain hydrometers designed for this work, and the hydrometer with a projecting stem is, of course, out of the question for third or fourth decimal place work. The pycnometer and the very sensitive Westphal balance are the only common instruments which approach the chain hydrometer in sensitivity and accuracy for alcohol determinations, but their time-consuming characteristics make them unsuitable for routine work.

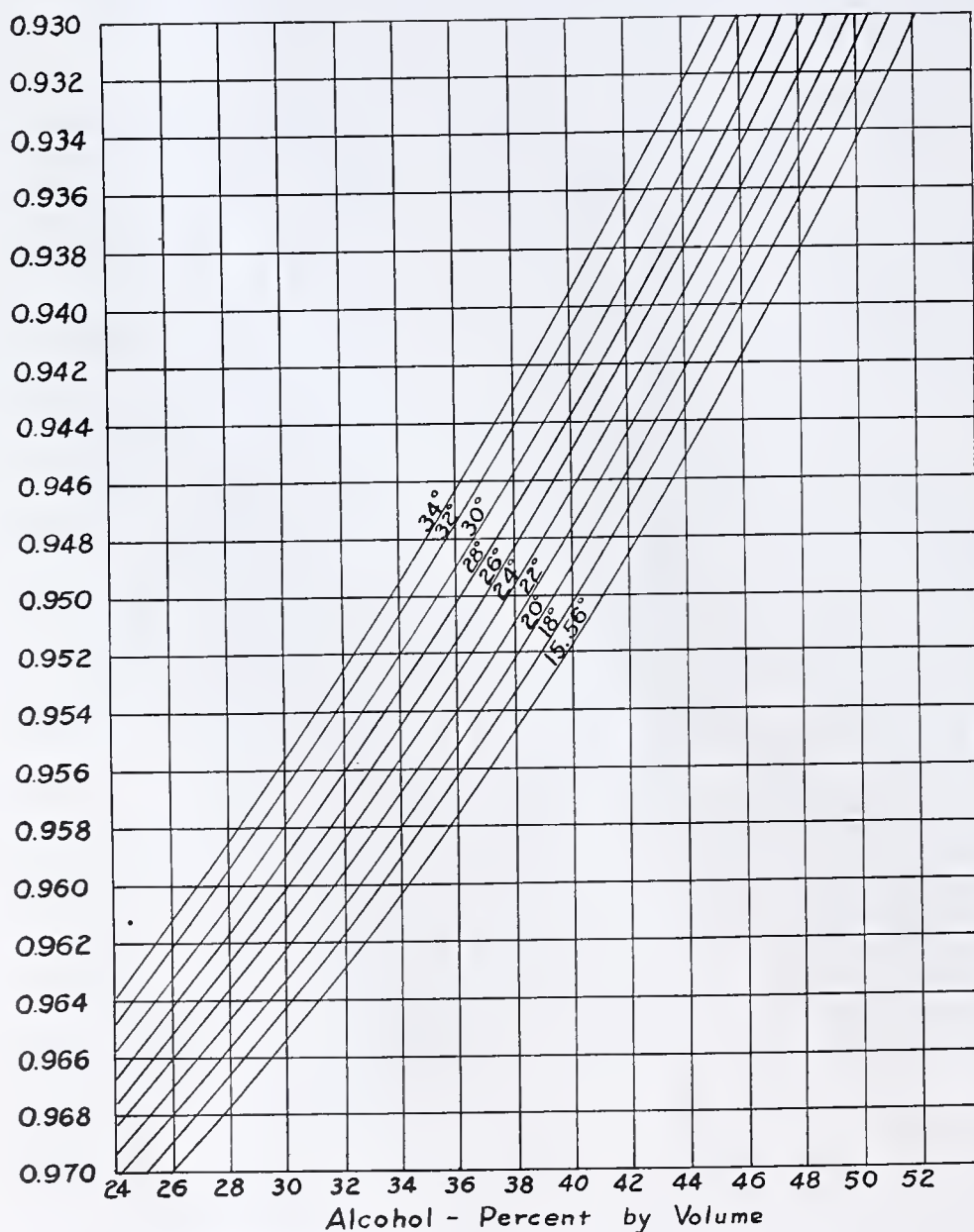


FIGURE 2. ALCOHOL-WATER TEMPERATURE CHART



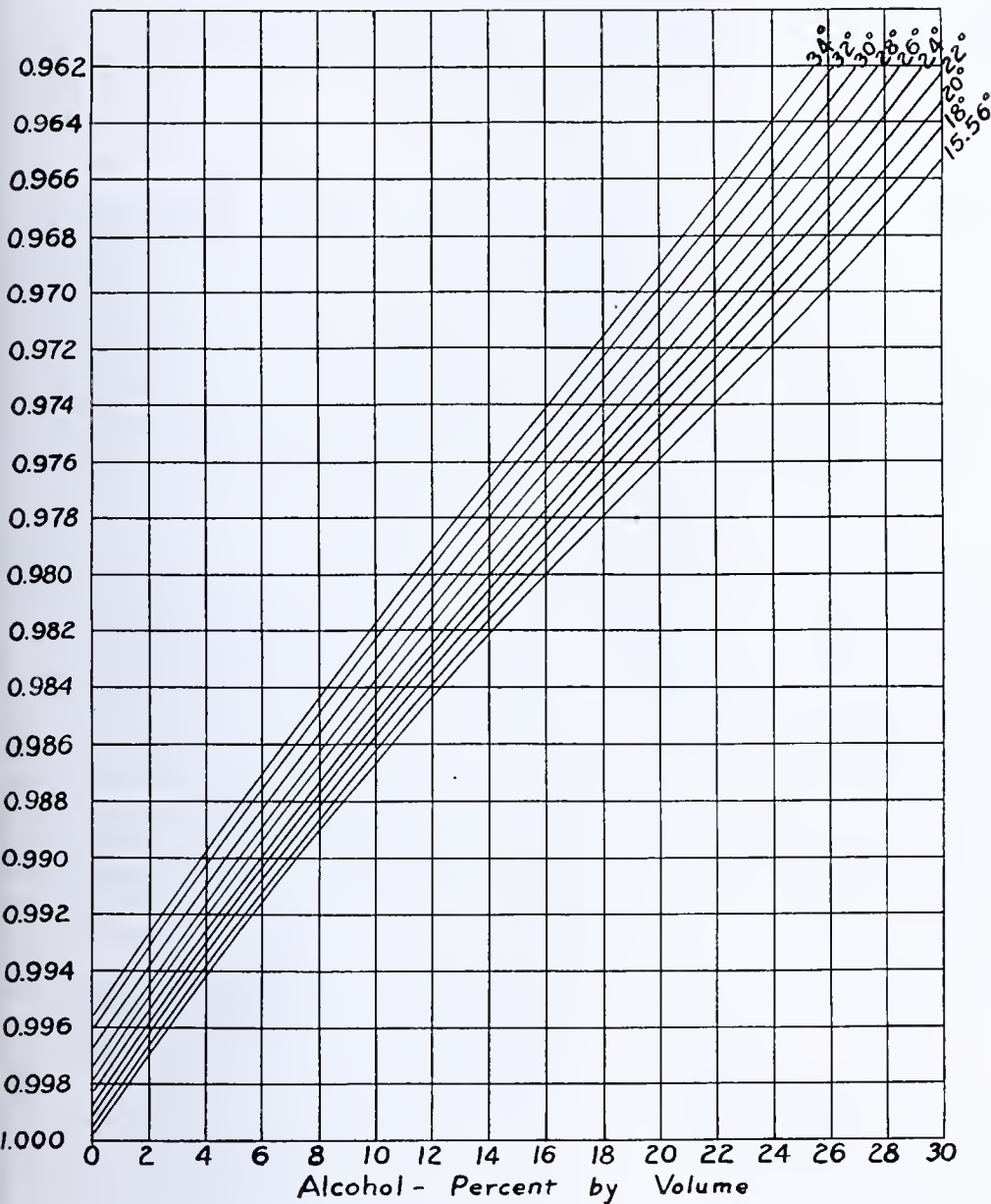


FIGURE 3. ALCOHOL-WATER TEMPERATURE CHART

liquid drained out through the stop-cock. This could be done by an ordinary workman without fear of damage to the delicate instrument, since he would not have to handle it at all. Many other industrial applications of this valuable instrument will come to mind on brief consideration.

Summary

The chain hydrometer, a sensitive and accurate instrument for the measurement of the density of liquids, has been successfully applied to the determination of alcohol in pharmaceutical liquids. It has significant advantages over other instruments for this purpose, mainly because it saves time without sacrifice of accuracy. Other industrial applications are suggested.

Alcohol-water temperature charts are described and illustrated, by means of which chain hydrometer readings or pycnometer weights at room temperature can be converted directly to alcohol percentages at the official temperature.

Acknowledgment

Appreciation is extended to C. W. Foulk for the initial inspiration and many helpful contributions he has made to this work, and to T. H. Rider for his valuable comments and suggestions.

The patent rights on the chain hydrometer are owned by the Kauffmann-Lattimer Company, Columbus, Ohio, which has generously given the author permission to make and use the hydrometers described in this paper.

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- (12) *Ibid.*, p. 604.

RECEIVED June 6, 1938. This is the third paper in a series on the "Determination of Alcohol in Pharmaceutical Liquids." For the first two, see *J. Am. Pharm. Assoc.*, **25**, 313, 982 (1936).

The chain hydrometers used here have surpassed the most optimistic expectations with respect to their continued accuracy over a long period of time. They have held their original calibrations for over 4 years of daily use. Literally thousands of alcohol determinations have been carried out with their help and they have shown no indication of change in accuracy or sensitivity during that time.

The chain hydrometer also has other important applications in chemical manufacture. Certain processes require careful density control and it often saves time to design special hydrometers for liquids which must undergo frequent density measurements. In one instance, a particularly disagreeable lachrymator was used in a manufacturing process. Density was an important factor in the control of this liquid, and making pycnometer weighings was an unpleasant task with such a substance. A special chain hydrometer solved the problem, for the entire manipulation was then carried out in a fume hood.

The greater sensitivity and accuracy of the chain hydrometer give it distinct advantages in the control of alcohol recovery in pharmaceutical manufacture and in the fermentation industries. A properly designed chain hydrometer, securely fastened to a wall in the plant and with a stopcock at the bottom of the outer tube which contains the sample, could take care of the work which is less accurately done at present with ordinary projecting stem hydrometers. The sample could be poured in at the top, the bulb allowed to come to rest, the reading and temperature taken, and the



# Use of a Palladium Tube in Gas Analysis

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A method of analysis for gas mixtures which consist largely of hydrogen and of small amounts of carbon monoxide, nitrogen, methane, and higher hydrocarbons is described. The higher molecular hydrocarbons are frozen at  $-180^{\circ}\text{C}$ . and the hydrogen is removed by diffusion through a palladium tube at  $300^{\circ}\text{C}$ . The carbon monoxide and the methane are then burned

over cupric oxide at  $250^{\circ}$  and  $800^{\circ}\text{C}$ ., respectively, and the products of combustion are frozen at  $-180^{\circ}\text{C}$ . The residue of the gas is nitrogen.

A study has been made of the limitation of the use of a palladium tube in the analysis of gases containing relatively large amounts of hydrogen and small amounts of carbon monoxide and methane.

IN THE course of an investigation of the effect of corona discharge on insulating oil, it was necessary to obtain an accurate knowledge of the composition of the generated gas. This type of gas mixture is largely hydrogen with a small amount, not over 5 per cent by volume, of methane and higher molecular hydrocarbons, a still smaller amount of carbon monoxide, not over 1 per cent by volume, and nitrogen, with no oxygen present. The conventional method of analysis (2), which was used during the initial part of the investigation, consisted of first separating the gases not condensable by liquid air from the gases which were condensable and then analyzing the noncondensable portion in a Burrell

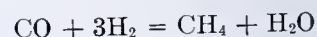
gas-analysis apparatus. No attempt was made to analyze the condensable portion because its volume was too small. Irregularities in the results of these analyses were due to two causes: (1) Small amounts of the gas dissolved in the absorbing solutions; (2) some of the methane burned with the carbon monoxide and hydrogen over cupric oxide at  $275^{\circ}\text{C}$ ., probably as a result of the excessive heat generated by the combustion of the relatively large amount of hydrogen.

To avoid such irregularities, a new procedure has been developed which uses a physical method to determine hydrogen and which eliminates carbon dioxide by freezing rather than by absorption in a water solution. This procedure involves the following steps:

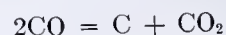
1. Elimination of all constituents condensable at liquid air temperature ( $-180^{\circ}\text{C}$ ).
2. Removal of the hydrogen by diffusion through a palladium tube.
3. Burning the carbon monoxide with cupric oxide at  $250^{\circ}\text{C}$ . and condensing at  $-180^{\circ}\text{C}$ . the carbon dioxide thus formed.
4. Burning the methane with cupric oxide at  $800^{\circ}\text{C}$ . following the method described by Rassfeld (6).
5. Measuring the amount of nitrogen left.

With regard to the first step, Mulders and Scheffer (4) proved that from a mixture of hydrogen, methane, and ethane the methane and hydrogen can be removed by cooling this mixture to the temperature of liquid air, which freezes the ethane, and then pumping off the hydrogen and methane by means of a Toepler pump.

As to the second step, Lombard and Eichner (3) stated that hydrogen alone will diffuse completely through a palladium tube above  $260^{\circ}\text{C}$ . The presence of carbon monoxide or methane with the hydrogen leads to irregularities in the diffusion of hydrogen through palladium. Sabatier and Senderens (7) found that carbon monoxide in the presence of a large amount of hydrogen is reduced to methane at a temperature between  $230^{\circ}$  and  $400^{\circ}\text{C}$ . according to the equation:



They also observed that above about  $300^{\circ}\text{C}$ . (but not markedly below about  $400^{\circ}\text{C}$ .) carbon monoxide decomposes according to the equation:



Coquillon (1) reported that, when hydrocarbons are passed over heated palladium, they are decomposed into carbon and hydrogen.

Before diffusion through palladium could be safely used for quantitative removal of hydrogen from the other gases

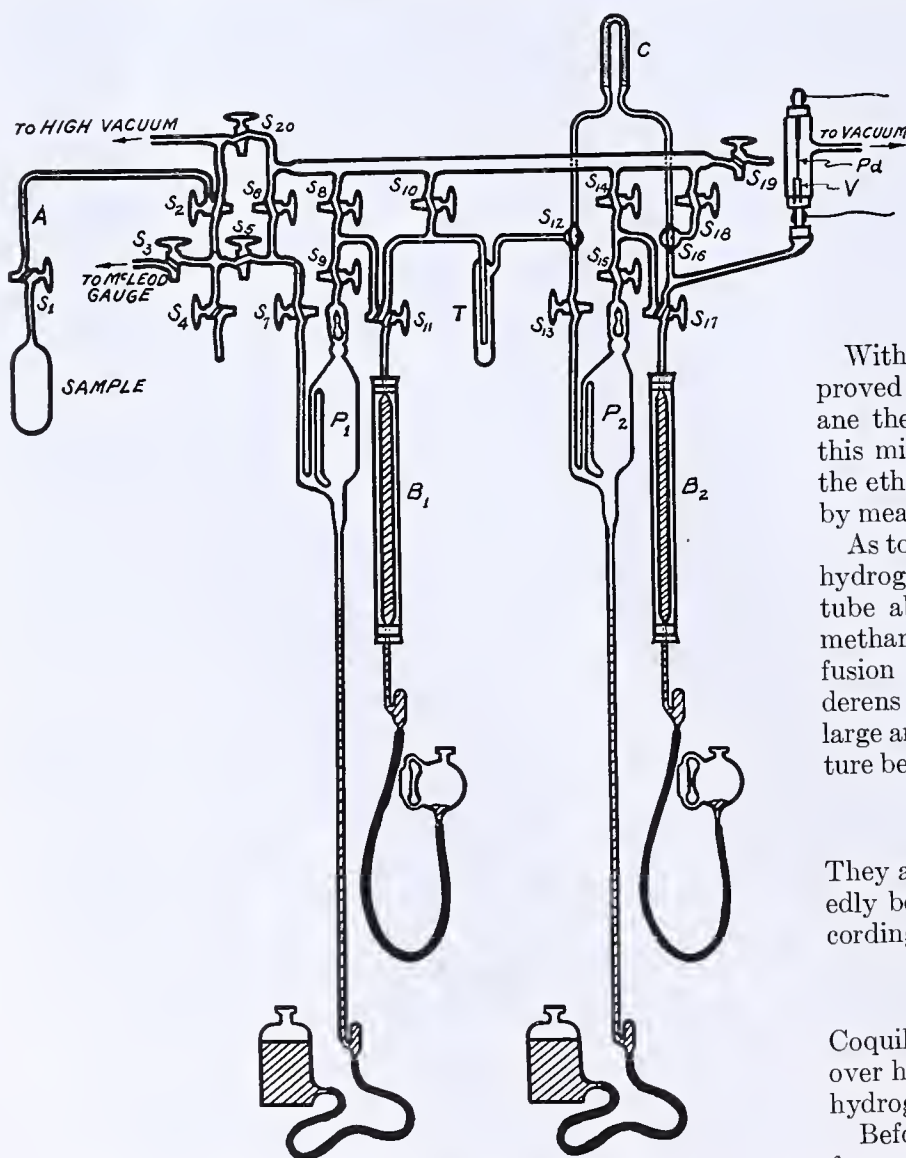


FIGURE 1. GAS-ANALYSIS APPARATUS



present, it was necessary to determine the concentration range of carbon monoxide and of methane through which the above-mentioned reactions would not vitiate the accuracy of the analysis.

### Apparatus

The gas-analysis apparatus in its present state of development consists essentially of the following parts as shown in Figure 1: a gas sample container, two Toepler pumps, two gas-measuring burets 76 cm. long and of 100-ml. capacity, with 0.2-ml. graduations, a condensation tube cooled by liquid air, a palladium tube, and a quartz tube containing cupric oxide. All these parts, the necessary stopcocks, and a McLeod gage are fused together, forming a vacuum-tight apparatus. Additional equipment includes a Cenco Hyvac pump, a mercury condensation pump, and vacuum flasks for holding liquid air.

The two Toepler pumps,  $P_1$  and  $P_2$ , are hand-operated. By means of  $P_1$  the gas sample is pumped from the container into the water-jacketed buret,  $B_1$ , where the volume of the gas sample is measured. From  $B_1$  the gas sample passes into the condensation tube,  $T$ . This tube is approximately 20 cm. long and is made of glass tubing of 16-mm. outside diameter, into which an inlet tube of about 7-mm. outside diameter is sealed. The construction is such that a gas sample, upon entering the condensation tube, passes through the inlet tube nearly to the bottom of the condensation tube and then rises in close contact with the outer wall to the outlet.

From the condensation tube, the uncondensed gas is pumped by the Toepler pump,  $P_2$ , into the water-jacketed buret,  $B_2$ , similar in design to  $B_1$ . The hydrogen in this gas is then quantitatively removed by absorption and diffusion through an electrically heated palladium tube,  $Pd$ . This tube, which is similar in principle to the one described by Paneth (5), is shown in detail in Figure 2. The palladium tube proper has a 2-mm. outside diameter and a 0.1-mm. wall, is 3.8 cm. long, and is closed at the upper end and sealed at that end to a copper rod, 3.2 mm. in diameter. At the other end this tube is open and sealed to a copper tube of 7.5-mm. outside diameter. The copper tube is attached by means of a Pyrex-copper seal to the gas-analysis system as shown in Figure 1. In order that the palladium tube shall not be exposed to a gas flame for a long time, a low-melting silver solder is used to join the copper and palladium tubes. This assembly is placed in a glass tube which is kept evacuated to prevent the palladium from oxidizing while hot, and the palladium tube is heated by passing current through it. This current is taken from the secondary of a current transformer having a ratio of ten to one. The primary is connected in series with a rheostat to a 110-volt alternating current source.

After the hydrogen has diffused through the palladium tube, the remaining gases—carbon monoxide, methane, and nitrogen—are introduced into the quartz tube,  $C$ , of 8-mm. outside diameter containing cupric oxide. This quartz tube is connected with the Pyrex tubing by means of two quartz-to-Pyrex graded seals and is heated by thermostatically controlled heaters.

### Procedure

After the sample container, closed by stopcock  $S_1$ , has been fused to the Pyrex tube at  $A$ , the whole system shown in Figure 1, except the sample container, is evacuated by opening stopcock  $S_{20}$  to the high-vacuum source. During the evacuation, all the stopcocks except  $S_1$ ,  $S_4$ , and  $S_{19}$  are open. After an absolute pressure of 1 micron or less is obtained, as indicated on the McLeod gage, stopcocks  $S_3$ ,  $S_6$ , and  $S_8$  are closed; three-way stopcock  $S_2$  is turned so that the gas can enter Toepler pump  $P_1$ ; and three-way stopcock  $S_{11}$  is turned to such a position that the gas can pass from  $P_1$  into buret  $B_1$ .  $S_1$  is now opened and  $S_7$  is closed.

The gas in  $P_1$  is forced from  $P_1$  into  $B_1$  by raising the mercury in  $P_1$  until it reaches stopcock  $S_9$ . Then  $S_9$  is closed, and the mercury level in  $P_1$  is lowered to permit more gas to enter  $P_1$  through stopcock  $S_7$  which is again opened. After closing  $S_7$ , the mercury in  $P_1$  is raised to force the gas admitted to  $P_1$  into  $B_1$  after opening stopcock  $S_9$ . This pumping is repeated until all the gas has been pumped from the sample tube, as indicated by a constant volume in  $B_1$ . Stopcock  $S_{10}$  and three-way stopcock  $S_{12}$  are then closed, and the gas from buret  $B_1$  is forced into the liquid-air condensation tube,  $T$ , whereupon  $S_{11}$  is closed. Five minutes later,  $S_{14}$  is closed, and  $S_{12}$  is turned so that the uncondensed gas can flow from condensation tube  $T$  through  $S_{13}$  into  $P_2$ . From  $P_2$  the gas is pumped into buret  $B_2$  through  $S_{15}$  and three-way stopcock  $S_{17}$ . To prevent the mercury in  $P_2$  from flowing into  $T$ ,  $S_{13}$  is closed each time the mercury is raised in  $P_2$ .

After all the uncondensed gas has been pumped from  $T$ , the gas volume is measured in  $B_2$ , taking into account the volume of the calibrated capillary tubing connecting  $S_{14}$ ,  $S_{15}$ , and  $S_{17}$ .

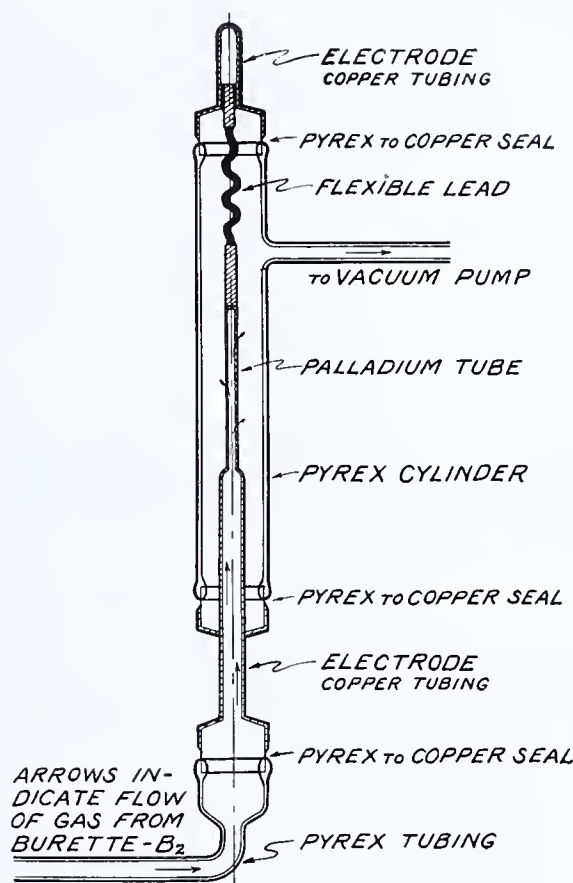


FIGURE 2. PALLADIUM TUBE

Upon closing  $S_{16}$  and turning  $S_{17}$  to the proper position, the gas is admitted from  $B_2$  to the palladium tube,  $Pd$ , which is heated to about 300° C. to allow the hydrogen to diffuse through. This tube, together with its connections, has a known volume. The temperature of the tube is determined from the ammeter readings taken in the electrical circuit and from calibration data. The gas which is left above buret  $B_2$  in the calibrated tube connecting stopcocks  $S_{14}$ ,  $S_{15}$ , and  $S_{17}$  must also be transferred to the palladium tube. In order to do this, the mercury in  $B_2$  is raised to stopcock  $S_{17}$ ;  $S_{17}$  is closed; and after lowering the mercury again in  $B_2$ ,  $S_{17}$  is opened toward the capillary tube containing the additional gas. This gas is drawn into  $B_2$ , from which it is transferred to the palladium tube by turning  $S_{17}$  and raising the mercury in  $B_2$ . After all the hydrogen has diffused through the palladium tube, as shown by a constant volume reading in  $B_2$  or its calibrated extension, the palladium tube is allowed to cool and the volume of gas is measured. The difference between this volume and the volume before diffusion of the hydrogen through the palladium tube is recorded as that of hydrogen.

In order to determine the carbon monoxide in the remaining gas, three-way stopcock  $S_{12}$  is turned to the proper position to communicate between the cupric oxide tube,  $C$ , and condensation tube  $T$ . Three-way stopcock  $S_{16}$  is next opened in such direction that the remaining gas passes into the cupric oxide tube,  $C$ , which is maintained at 250° C. The carbon dioxide formed is solidified in  $T$ , and the volume of gas free from carbon dioxide is measured after the gas has been pumped from  $T$  into  $B_2$ . From  $B_2$  the cycle is repeated until the buret reading remains constant. This indicates the removal of all carbon monoxide. Usually two cycles are sufficient to obtain a constant buret reading.

Only methane and nitrogen are now left in  $B_2$ . The temperature of cupric oxide tube  $C$  is now raised to 800° C. and the gas in  $B_2$  is passed through the cycle mentioned above until a constant volume is obtained, which indicates that all the methane has been burned. A small amount of oxygen is set free from cupric oxide during this methane combustion at 800° C., but is made to recombine with the copper by passing the remaining gas over the cupric oxide at a lower temperature (250° C.).

The final volume is then measured in  $B_2$ , and the difference between this volume and the volume left after combustion of the carbon monoxide is that of methane. The remaining volume is recorded as that of nitrogen.



## Testing the Method

The gases used for testing the accuracy and limitations of the method were made as follows:

**HYDROGEN.** Pure dry hydrogen was prepared by allowing commercial hydrogen to diffuse through a heated palladium tube into a glass storage bottle evacuated to 1 micron of mercury. Analysis of this gas in a Burrell gas-analysis apparatus showed it to be free from impurities.

**METHANE.** The methane was prepared by dropping methyl iodide dissolved in an equal volume of 95 per cent ethyl alcohol into a flask containing a large quantity of zinc-copper couple. The gas was passed through two traps, cooled by a carbon dioxide-acetone mixture, into a gas storage bottle. Analysis by means of a Burrell gas-analysis apparatus gave the following composition:

CH<sub>4</sub>, per cent by volume, 99.5  
N<sub>2</sub>, per cent by volume, 0.5

**CARBON MONOXIDE.** The carbon monoxide was prepared in an all-glass system according to the method of Thompson (8). The composition of this gas, as determined by means of a Burrell gas-analysis apparatus, was:

CO, per cent by volume, 99.8  
N<sub>2</sub>, per cent by volume, 0.2

**SYNTHETIC MIXTURES.** In order to find the concentration range of carbon monoxide and of methane for which the method gives accurate results, gas mixtures were prepared containing hydrogen and amounts of carbon monoxide and methane which were increased in small steps in successive samples.

These gas mixtures, ranging in volume from 30 to 80 ml., were measured in a 100-ml. buret graduated in 0.2 ml. and were then analyzed by the new method. If the volume of gas obtained by analysis agreed within 0.1 ml. with the volume of gas taken, the method was considered accurate within the limits set by the accuracy of the gas-measuring buret.

TABLE I. MIXTURES OF HYDROGEN AND CARBON MONOXIDE

Sample No.	Constituents Taken, Per Cent by Volume		Constituents Found, Per Cent by Volume			Temperature of Palladium ° C.
	Hydrogen	Carbon monoxide	Hydrogen	Carbon monoxide	Methane	
1	96.0	4.0	96.0	4.0	0.0	300
2	94.1	5.9	94.1	5.9	0.0	300
3	92.2	7.8	92.2	7.8	0.0	300
4	91.9	8.1	91.9	8.1	0.0	350
5	91.6	8.4	91.6	8.4	0.0	260
6	90.9	9.1	90.9	9.1	0.0	350
7	84.3	15.7	84.3	15.4	0.3	300

Table I shows the results of analyses of mixtures containing hydrogen and carbon monoxide. It was found that gas mixtures of this type containing up to 9 per cent by volume of carbon monoxide could be analyzed accurately by this new method.

TABLE II. MIXTURES OF HYDROGEN AND METHANE

Sample No.	Constituents Taken, Per Cent by Volume		Constituents Found, Per Cent by Volume		Temperature of Palladium ° C.
	Hydrogen	Methane	Hydrogen	Methane	
1	98.3	1.7	98.3	1.7	300
2	94.9	5.1	94.9	5.1	300
3	94.6	5.4	95.1	4.9	300
4	89.0	11.0	92.8	7.2	300

In order to ascertain whether an increase in the temperature of the palladium tube promoted the reduction of carbon monoxide to methane, three gas mixtures of almost identical composition were prepared (Table I, samples 3, 4, and 5). It was found that an increase in temperature of the palladium from 260° to 350° C. did not cause a reduction of carbon mon-

oxide to methane in an excess of hydrogen if the carbon monoxide content of the gas mixture was less than 9 per cent by volume.

The presence of 4 per cent or more of carbon monoxide rapidly reduces the diffusion rate of hydrogen through palladium. The time required for the complete diffusion of the hydrogen in sample 1 was 98 minutes as compared with 270 minutes for an equal volume of hydrogen in sample 3.

The results of analyses of synthetic mixtures of hydrogen and methane are shown in Table II. Apparently the palladium at 300° C. promotes decomposition of the methane into hydrogen and carbon, as suggested by Coquillon (1). In the results of the analyses made on samples 3 and 4, the hydrogen percentage is high and the methane percentage is low. If the methane content is less than 5 per cent by volume, the decomposition of the methane is not sufficient to cause measurable errors in the determination of the constituents.

TABLE III. MIXTURES OF HYDROGEN, CARBON MONOXIDE, AND METHANE

Sample No.	Constituents Taken, Per Cent by Volume			Constituents Found, Per Cent by Volume			Temperature of Palladium ° C.
	Hydrogen	Carbon monoxide	Methane	Hydrogen	Carbon monoxide	Methane	
1	94.7	0.9	4.4	94.7	0.9	4.4	300
2	92.8	1.6	5.6	92.8	1.6	5.6	300
3	89.4	0.9	9.7	89.4	0.9	9.7	300
4	86.6	4.3	9.1	87.2	4.0	8.8	300
5	86.2	7.4	6.4	92.6	6.9	0.5	300
6	84.4	9.1	6.5	93.3	4.0	2.7	300

Table III contains results of analyses of synthetic mixtures of hydrogen, carbon monoxide, and methane. A comparison of the results for the first three samples with those for the remaining samples indicates that the presence of over 1.5 per cent by volume of carbon monoxide in a gas mixture of this type causes errors not only in the percentage of hydrogen but also in the percentages of carbon monoxide and methane. If there is less than 1.5 per cent by volume of carbon monoxide in a gas mixture containing not over 5 per cent of methane and a relatively large amount of hydrogen, each of the constituents can be determined accurately by the proposed method.

## Conclusions

The described method can be used successfully for the analysis of gas mixtures having a volume of 30 to 80 ml., such as are generated from hydrocarbons subjected to corona discharge. These gas mixtures usually contain a large amount of hydrogen, not over 1 per cent by volume of carbon monoxide, and not over 5 per cent by volume of methane. The results of analysis are accurate within the limits of accuracy of a 100-ml. gas buret graduated in 0.2-ml. divisions.

Removal of the hydrogen from the gas sample before the combustion of carbon monoxide with cupric oxide at 250° C. improves the accuracy of the determination of carbon monoxide and of methane in the remaining gas mixture.

No liquid reagents are employed, thus eliminating the error due to the solution of gases in liquids and to the change in volume which occurs when a dry gas is placed in contact with a water solution.

A palladium tube cannot be used promiscuously for the quantitative determination of hydrogen in gas mixtures. The presence of over 5 per cent by volume of methane in a hydrogen-methane mixture causes low results for methane and high results for hydrogen, due to the decomposition of methane in contact with palladium at 300° C. Accurate quantitative determinations of hydrogen can be made by the palladium tube diffusion method in a hydrogen-carbon mon-



oxide mixture containing up to 9 per cent by volume of carbon monoxide. The diffusion rate of hydrogen through palladium decreases rapidly if more than 4 per cent by volume of carbon monoxide is present in the gas sample. Gas mixtures containing less than 1.5 per cent by volume of carbon monoxide and less than 5 per cent by volume of methane with a relatively large amount of hydrogen can be accurately analyzed by the described method. If higher percentages of carbon monoxide and methane are present, however, the results for hydrogen are high and those for carbon monoxide and methane are low.

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## A Continuous Extractor Using Hot Solvent

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IN THE course of a series of experiments on the constitution of certain resins, it became necessary to carry out an extraction with hot solvent upon several kilograms of tarry material. A cursory search of the available literature failed to disclose any suitable type of extractor capable of handling large quantities of material and at the same time using boiling solvent. The apparatus described herein is designed to meet the very real need for such an extractor.

This type of extractor possesses the following advantages over the conventional designs:

It may be attached to any flask, thus eliminating the transfer of material from another vessel.

It uses solvents at temperatures as high as the boiling point, where frequently the dissolving power is greatly enhanced.

It increases the surface of contact between solvent and material to be extracted, by reason of the act of boiling and because of the rapid influx of hot vapor.

Channeling and filter clogging are entirely avoided for the same reasons, permitting the apparatus to be used in the extraction of adhesive, semisolid tars, or gelatinous substances.

The flow of solvent is rapid, varying from 20 to 50 cc. per minute.

It is capable of handling much larger quantities of material than the conventional types of extractors.

It is inexpensive, and may be constructed from ordinary laboratory materials by the most inexperienced glass blower.

The action is continuous and entirely automatic, requiring no attention whatsoever.

The operation of the extractor will be made clear by the accompanying diagram.

Solvent, boiling in flask *A*, produces vapors which are forced up tube *B* into flask *C* which contains the material to be extracted together with a suitable quantity of solvent. The level of the solvent is controlled by the height of tube *E* above the bottom of the flask.

The rapid influx of vapor, which is under a slight pressure, violently agitates the contents of flask *C* and soon heats them to the boiling point. The hot solution of extract is forced through the filtering device, *J*, and proceeds through tube *E* to side-arm vessel *F*. Excess vapor which has not been condensed by the microcondenser, *K*, or by passage through the solution, is condensed in *G*, and descends, together with the solution of extract, into flask *A*, where the extracted material accumulates.

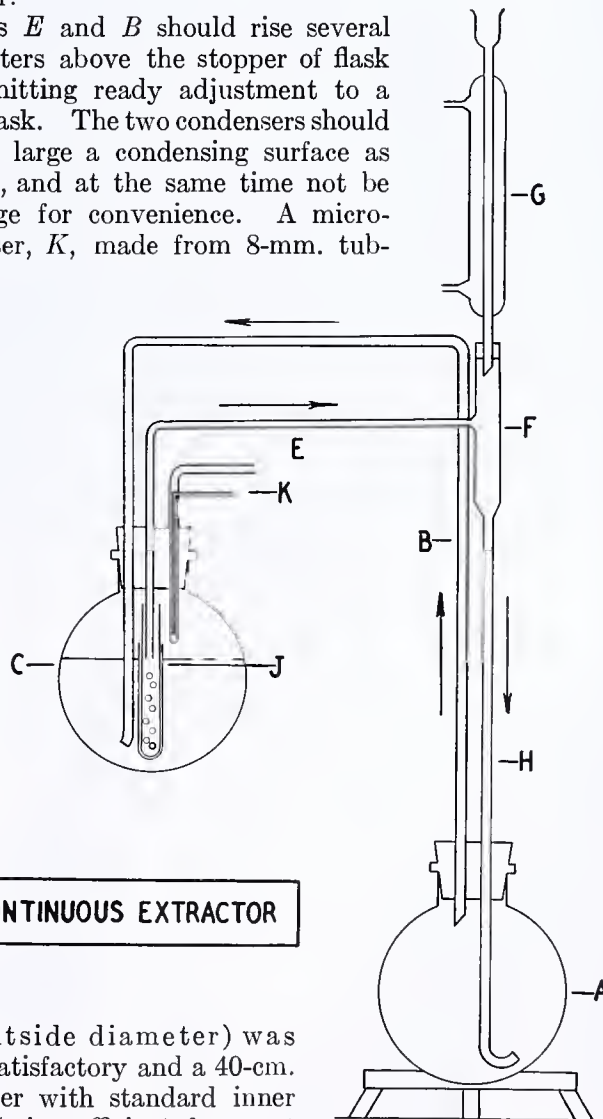
Filtering device *J* consists of a length of large-diameter glass tubing sealed at the bottom, and perforated along the lower half of its length. A close-fitting extraction thimble is slipped over the perforated portion and the whole is placed over tube *E* as shown. The filter paper may be protected by a wrapping of cloth, for use with alkaline or corrosive solutions.

### Dimensions

Dimensions of the apparatus may be varied to suit the needs of the moment. It is necessary, however, to have tube *H* of sufficient length to ensure an ample hydrostatic head

for the descending solution. A length of 53 cm. with an attendant difference of 32 cm. in level of the liquid in the two flasks was found advisable. The hydrostatic head, of course, depends on the density of the liquid, the height necessary being here governed by the fineness of the filter.

Tubes *E* and *B* should rise several centimeters above the stopper of flask *C*, permitting ready adjustment to a larger flask. The two condensers should have as large a condensing surface as possible, and at the same time not be too large for convenience. A microcondenser, *K*, made from 8-mm. tub-



ing (outside diameter) was found satisfactory and a 40-cm. condenser with standard inner tube, *G*, is sufficient for most solvents.

If the two flasks have a capacity of not over 1 liter, 8-mm. tubing is suitable for *E*, *B*, and *H*. The perforated filter support is of such diameter that standard extraction thimbles will fit tightly over it. Eighteen-millimeter tubing was successfully used with standard 19-mm. paper thimbles.

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# Laboratory Columns Packed with Silicon Carbide

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Tests on distillation columns packed with ordinary lump silicon carbide indicate that this cheap, chemically inert material may properly be classed with the most efficient column packings now in use.

No special care is required in handling, and a fouled packing can be cleaned with

boiling acid cleaning solutions if necessary. Since distillations may be made with equal impunity using organic bases, corrosive sulfur compounds, or unstable halides, silicon carbide-packed columns are particularly recommended for general laboratory use.

IN A PREVIOUS article (8) the authors described a  $3.15 \times 150$  cm. laboratory distillation column packed with 3- to 6-mesh silicon carbide, used for the successful isolation of 1-pentene and 1-hexene as chemical raw materials from cracked gasoline. The tests described below indicate that this column compares favorably in efficiency with the best of the recently developed packed columns, and this serves to direct further attention to this cheap, sturdy, and chemically inert packing material.

The chief advantage of silicon carbide over these other packings, some of which are equally efficient, lies in the fact that it may be used for almost any type of distillation. The use of 60-mesh silicon carbide to coat the walls of an efficient laboratory column of special design was first noted by Midgley (9), who also suggested its use as a column packing. Unfortunately, however, its value as a packing material in the ordinary sense does not seem to be widely appreciated.

Columns of this type have been used in these laboratories for a wide variety of distillations, including organic sulfides, polymerizable or gum-forming hydrocarbons, and volatile inorganic halides. This particular column was used for the vacuum distillation of several large batches of crude olefin dibromides, which involved a certain amount of decomposition and tar formation due to the presence of small amounts of tetrabromides as impurities; after this use the packing was restored to practically its original efficiency by simple solvent refluxing. The same column was also used for the separation of alpha- and gamma-picoline and quinaldine from crude nitrogen bases (1). In general, simple solvents are used to clean up the packing after one of these general utility distillations. When pronounced decomposition occurs in a small batch distillation, the packing is cheap enough to be discarded after use, although it may be boiled with nitric acid or chromic acid cleaning solution if desired.

There is no major difference between the various types of silicon carbide available on the market, although there is a slight difference in favor of a fine-grained crystalline form, with a fairly open or porous structure. Results discussed below also indicate that there may be a distinct advantage in throughput when using 3- to 6-mesh material instead of straight 6-mesh, but this point is still subject to direct experimental confirmation. Silicon carbide-packed columns are found to operate most efficiently at the maximum throughput, just short of the flooding point.

## Test Data

The all-Pyrex laboratory column mentioned above and used for the tests was modeled after Peters and Baker (11), with an insulating dead-air jacket and a second insulating

heated-air jacket. The test data given in Table I were obtained by using a mixture of benzene and ethylene chloride (4) on total reflux under substantially adiabatic conditions. The test mixture used forms a nearly ideal solution with components boiling  $3.39^\circ$  apart (12), and the molar compositions of the still pot liquid,  $x_0$ , and distillate,  $x_n$ , analyzed by refractive index may be substituted in the formula of Beatty and Calingaert (2) to calculate the number of theoretical plates,  $n$ :

$$n = (\log (1 - x_n) x_0 / (1 - x_0) x_n) / \log R$$

The theoretical value of 0.045 for  $\log R$  used here is preferred to the experimental value of 0.036 which may be calculated from published data in the literature (10). The theoretical value is taken from direct comparative measurements made at the Bureau of Standards on the relative volatility of pure benzene and ethylene chloride (12). The smaller experimental value of  $\log R$  would increase the rated efficiency of the columns by 25 per cent, and there is some indication that the binary mixture at its boiling point may depart slightly from ideality in this direction. However, the experimental data concerned are not mutually consistent throughout, and since the solution is very nearly if not precisely ideal, the authors prefer to use the conservative theoretical value (3). The benzene and ethylene chloride used were purified as recommended by Bruun and Schicktzan (4), and gave refractive indices of 1.4977 and 1.4422, respectively, as measured on an Abbe refractometer at  $25.2^\circ \text{C}$ .

TABLE I. TEST DATA

Packing (3- to 6-Mesh)	$n_{D}^{25}$		Mole % $\text{C}_2\text{H}_4\text{Cl}_2$		$n$	H. E. T. P. Cm. (Inches)
	Head	Pot	Head	Pot		
Silicon carbide						
Ordinary, porous	1.4890	1.4639	14.72	59.53	20.7	7.6 (3.0)
Ordinary, used	1.4887	1.4658	15.23	56.03	18.9	8.4 (3.3)
Crystalline	1.4882	1.4640	16.08	59.35	19.6	8.1 (3.2)
Cracked glass	1.4792	1.4680	31.70	51.98	8.2	20.9 (8.2)
Fritted glass	1.4826	1.4648	25.72	57.87	13.3	12.2 (4.8)

The two varieties of silicon carbide used were broken up from 2.5-cm. (1-inch) lumps, using a hatchet to avoid too much crushing. The ordinary or porous variety was prepared from one of the more fragile grades available on the market. Operating at the maximum total reflux capacity of 75 cc. of liquid reflux per minute, the column gave the equivalent of 20 theoretical plates. The equilibrium value for the distillate composition was approached in the first 2 hours, and after 3 hours on total reflux no further change in the product occurred in a 10-hour test. This packing was used for 500 hours of olefin dibromides under 10- to 85-mm. absolute pressure. At the end of this period the column was partially choked with accumulated deposits; it was refluxed with alcohol and then with some of the test mixture, dried, and tested again. Superficial inspection showed that there was still some tar or coke left on the packing after this simple solvent treatment, but the column efficiency showed relatively little drop as compared with the same packing before use.

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The second variety of silicon carbide tested was a special large-grained and less porous sample consisting mostly of aggregates of 2- to 4-mm. crystals. There is a minor advantage in the porous variety with small crystals, but the difference is not great enough to be important. Subsequent tests with 6-mesh silicon carbide purchased on the open market have shown this material to be equally satisfactory, as measured in terms of the height equivalent to a theoretical plate (H. E. T. P.).

The tests with the glass samples were made to determine whether the sharp edges and points of this material would make it also a good packing medium. The results show that the fritted glass is efficient enough to compare favorably with packing media of a number of commercial types. This material, prepared by running molten glass from a furnace into a rapid stream of water, has small flat surfaces with sharp edges and a number of internal cracks, but relatively few points. The cracked glass prepared from cullet in a jaw crusher has a few sharp edges and relatively large flat surfaces. The results show a definite increase in efficiency from cracked glass through fritted glass to crystalline and porous silicon carbide, which is quite in line with Miss Farnham's theory that silicon carbide owes much of its efficiency to sharp edges and points exposed (6). This same conclusion has been independently confirmed in a recent industrial gas-absorption unit, where the fractionating efficiency of an absorption column was found to be very much greater when using small rough die castings than when using exactly the same castings after they had been tumbled to remove the sharp edges and corners (5).

TABLE II. COMPARISON OF PACKINGS

Packing	Total Hours	Dis- tillation Rate Liters/hr.	$\Delta P$ Mm.	$n$	H. E. T. P. Cm. (Inches)	Test Number (7)
6-mesh silicon carbide	36	2.2	9	51	5.1 (2.0)	X-5
Maximum	42	3.7	51	57	4.6 (1.8)	X-7
0.23-cm. (0.094-inch) steel single-turn helices	13	4.7	13	51	5.1 (2.0)	XVI-9
Maximum	29	11.0	33	46	5.6 (2.2)	XVI-25
0.3-cm. (0.125-inch) carding teeth	67	4.6	6	52	5.1 (2.0)	XVII-29
Maximum	37	14.8	30	29	8.9 (3.5)	XVII-14
No. 19 A1 jack chain	49	3.7	2	24	10.7 (4.2)	VII-21
Maximum	53	14.0	13	19	13.7 (5.4)	VII-11
0.47-cm. (0.188-inch) A1 single-turn helices	39	4.1	2	23	11.2 (4.4)	XII-8
Maximum	21	19.3	22	26.5	9.7 (3.8)	XII-35

Efficiency tests were also run on a 7.5-cm. (3-inch) column of the Midgley type (9). This column was made up of fifty turns of a flat copper spiral in a total height of 47.5 cm. (19 inches), coated internally with 20- to 60-mesh silicon carbide. The column showed the remarkably low H. E. T. P. of 2.7 cm. (1.06 inches), but the maximum distillation rate without flooding was only 1.8 liters per hour, owing to the flat pitch of the spiral. This limits the practical usefulness of columns of this type, even though the column may have a large number of theoretical plates. However, this maximum distillation rate was more than doubled when the same column was used later for the fractionation of mixed hydrocarbons in the range of 1-hexene (8).

### Comparison with Other Packings

After the above tests were completed, a sample of 6-mesh silicon carbide purchased on the open market was included by Fenske, Lawroski, and Tongberg in a direct comparison with various metal packings for a study of distillation column packing materials (7). Their measurements were made in a jacketed 5-cm. (2-inch) Pyrex column with a 255-cm. (102-inch) packed section, using a test mixture of *n*-heptane and

methyl cyclohexane. The particular runs listed in Table II were recorded after ample time had elapsed for thermal equilibrium to be established in the relatively large packed section being tested. The data selected are arranged in the table in the order of the maximum liquid velocity which the packings were able to handle without flooding, on total reflux.

Table II shows the relative efficiency of the silicon carbide packing, but also points to a relatively low maximum distillation rate before flooding occurs. This may be due in part to the use of 6-mesh instead of 3- to 6-mesh material. The 150 × 3.15 cm. column (Table I) was used for olefin distillations from a 5-liter pot with a take-off rate of 300 cc. per hour at a reflux ratio of 15 to 1, which is a higher capacity than that indicated for the 6-mesh packing in Table II. The 3- to 6-mesh silicon carbide poured roughly into a 3.15-cm. column shows about 70 per cent free space, while the various wire packings show 80 to 90 per cent free space, depending somewhat on how carefully they are placed in the column. Further tests are planned to determine the optimum relation between packing size and column diameter in silicon carbide-packed sections of a given height.

### Discussion

The silicon carbide and metal packings in Table II show about the same H. E. T. P. at equilibrium under total reflux, but the wire packings allow either a higher take-off rate or an increased reflux ratio with columns of a given size. A direct comparison of the results in Tables I and II is not possible, since two different test mixtures were used, but it is at least apparent that there is no large loss in the efficiency of the silicon carbide in a large column. For most laboratory distillations, including the usual purification of chemical raw materials, the size of the column is not a major factor, and a column may be built of any suitable size, as long as a separation of the desired efficiency can be attained. In those cases where very small amounts of chemically stable material are to be distilled, or where time is a major factor, other packings with increased throughput may well be preferred if they are available. For routine laboratory distillations, which may at times include corrosive or unstable halides or sulfur compounds, the silicon carbide shows a distinct advantage, and it is therefore recommended for such general use.

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# The Research Laboratories of Mellon Institute

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**T**HIS article describes the elements of design, construction, and equipment of the research laboratories in the new Mellon Institute building, with the hope that this information will be of value to specialists who may have a similar task. The institute's facilities are devoted primarily to basic researches in the fields of chemistry and chemical engineering. Its fellowship system, by which scientific investigations are conducted for a large number of companies concerned with widely varying types of problems, makes necessary the provision of many small laboratory rooms for the use of one or several fellows, whereas in a company research organization larger laboratories might be utilized advantageously and would have lower constructional cost.

The institute's new home was erected entirely during the depression period from late in 1930 to early in 1937. Construction work was not pushed rapidly, and thus more than the usual time was available for study and perfection of the details of design and erection. A year's operation of the building has brought forth very few suggestions as to how the design of the rooms and equipment could be better suited to the purposes intended.

There are eight floors, the four upper floors containing the typical laboratories described here, the fourth or main floor the administrative offices, library, and museum, and the three lower floors the auditorium, special laboratories, shops, unit plants, and mechanical equipment. Over one hundred laboratories are provided on the upper floors; about one-third of their total area has been left unfinished for typical or special laboratories to be constructed when and as needed.

## Use of Models

Just as the architect used models of the exterior to determine architectural proportions, so the engineers employed models in designing the laboratories. A frame building was erected in which was constructed and completely equipped one each of the two types of standard laboratory rooms.

One of the first points brought to light was the visual appearance of the beam type of floor slab construction when the room contained fractional parts of bays, giving an uneven beam spacing on the ceiling. This discovery was made in time to change to the flat arch type. The size of the small laboratory (consisting of one bay) was satisfactorily fixed by the column spacing of the building, but the division of space between laboratory and office in the two bays comprising the large laboratory suite had to be worked out in the model.

Special furniture, of wood or of metal, was built for these rooms by several manufacturers, embodying suggestions as to the best methods of providing flexibility, simplicity, and utility. None of these, however, attained the goal set, par-

ticularly in regard to flexibility, and considerable original development was necessary before this problem was satisfactorily solved. The final result was a new type of laboratory furniture of extreme flexibility, consisting of a supporting structure composed of standard vertical and horizontal frames going together without bolts, screws, or nuts, and removable cabinets of uniform size.

In this model laboratory were also evolved the vertical wall slots, adjustable shelf brackets, a method of supporting service and drain pipes from the wall slots, and a new wiring trough and turrets for the benches. Special pipe fittings were devised, eliminating a number of screwed joints, and ceiling light outlets were located. Here also experimental fume hoods were built of plywood and subjected to extensive tests, which led to a new design of hood.

While the design of these standard laboratories was thought to have been well worked out on paper, it was found possible to make numerous improvements; and a practical means was created for getting helpful criticism from many laboratory workers who could not or would not study a drawing. The model laboratory building saved many times its cost; it certainly ensured a better design of the finished laboratories.

## Research Laboratories of the Institute

The typical research laboratories are, in general, of two sizes. There are a few variations from the floor plans (Figure 1), some three-window laboratories being without offices and some two-window laboratories having offices. Each standard two-window laboratory occupies a bay of the building and includes two laboratory benches along the side walls. The right-hand bench is shortened at the window end to make room for a special laboratory desk. A built-in clothes locker is also included.

Each standard large laboratory with its adjoining office (three windows in the laboratory and one in the office) occupies two bays. The furniture consists of a wall bench along each partition wall and a center bench connected to the window wall, with a large sink on the free end. The large laboratories are, wherever possible, located in pairs—one right- and one left-hand—with a common entryway and an entrance door for each laboratory. If it is desired to use the two laboratories separately, the entry is divided by a bank of clothes lockers. If the two rooms are to be connecting, the lockers are placed against the corridor wall, as shown in the floor plan, leaving a passageway. Recessed glass door cases for displays, storage of instruments, etc., are set in the corridor walls of the large laboratories in the area which would have been used as an entrance door if the two bays had been utilized for two small instead of one large laboratory.



The small laboratories vary in width from 11 feet 9 inches to 12 feet 2.25 inches, and the large laboratories from 17 feet 3.25 inches to 17 feet 11.5 inches. The depth of both types is the same and varies in different parts of the building from 18 feet 10 inches to 19 feet 2 inches.

**CONSTRUCTIONAL MATERIALS.** Glazed architectural terra cotta is used throughout the four laboratory floors and in most other parts of the building for corridor and room walls. The principal exception is in the case of the pilasters between windows and the walls beneath window sills in the standard laboratories.

The terra cotta blocks are of cream or light buff color, semidull finish, varying slightly in shade to prevent monotony, 16 × 8 inches in size, and laid horizontally with a  $\frac{3}{16}$ -inch tinted mortar joint. The base course of all terra cotta walls is chocolate brown to match the dark Sienna marble used around certain windows in the corridors and as a floor in the fire-extinguisher niches. Blocks in partition walls are 3 inches thick, glazed on one surface only. A double-faced partition wall is therefore about 6.5 inches thick. The jointing of the blocks was carefully done. Terra cotta is readily cut by a Carborundum saw and sufficient cuts were made so that few blocks smaller than half size were used in the walls. Special shapes were used where required to prevent unsightly jointing, and in the entryways of the large laboratory suites to receive the knobs of the office doors (Figure 1), to give the maximum space for passage when the rooms are used en suite.

Wall surfaces of glazed terra cotta are particularly appropriate for use in laboratories because they are easy to clean and free from attack by ordinary laboratory fumes. Ready cleanability is facilitated by the use of round corners and by a cove-base course. In a glazed terra cotta wall it is desirable to use large blocks, so that there will be as few mortar joints as possible. Such joints darken from wall washing and in time mar the beauty of the wall.

The window ends of the standard laboratories, composed of the pilasters between windows and the wall beneath the window sills, are constructed of removable Transite panels, 0.25 inch thick, finished with Vinylite paint to match the terra cotta and trimmed with aluminum molding strips. These panels conceal all service distributing pipes, drains, and conduits, yet render them readily accessible for repairs.

The laboratory floor is, of course, subject to more use and abuse than any other part of the room and hence the choice of a suitable material for this purpose has always been difficult. The ideal laboratory flooring material should have resistance to acids and alkalis, insolubility in organic solvents, freedom from indentation, and resiliency. No material possessing all these properties is known to the writer. Asphalt tile and mastic have been extensively used, but meet only the first requirement satisfactorily. Cork and rubber make the most resilient floors, but fall short on resistance to

acids and alkalis and insolubility in organic solvents. Ceramic tile, although not resilient, possesses the other properties to an admirable degree, and was therefore chosen. The tiles are 6 inches square by 0.5 inch thick, of a buff color and totally impervious. They are laid with a narrow mortar joint composed of high-silica cement, which is more resistant to acids than ordinary Portland cement. If acid is spilled on the floor, the joint can be regouted. To provide resiliency, loose corrugated rubber or link mats are used where needed.

The laboratory ceilings are plaster, painted with Vinylite paint. Diamond metal mesh was first securely tied to the tile slab and then scratch and brown coats of mortar composed of neat gypsum wall plaster were applied. The finish or skim coat was composed of properly soaked hydrated lime and pure white gypsum gaging plaster. This type of ceiling finish was selected after extensive tests with many types of plaster. It was found that, with the metal mesh, common patent or gypsum plaster could be used with less likelihood of falling, when soaked with water from the floor above, than any of the more expensive cement plasters. Furthermore, gypsum plaster does not craze and crack as do cement plasters.

The windows in the laboratories and throughout the building are made of anodic-finished aluminum extruded sections and glazed with 0.25-inch polished plate glass.

As shown in Figure 3, the windows consist of two outwardly swinging casement sashes, latching to a permanent mullion, beneath which is an inwardly swinging sash hinged at the bottom. The lower sash is held in any position by a friction device and admits air to the room without creating a draft, which would disturb a Bunsen flame on the laboratory bench. The casement sashes are controlled by a worm-and-wheel crank-operated device which will hold them open even against a strong wind, and are locked in the closed position by a lever handle on the center mullion which operates bars engaging three lugs on each sash. A handle in the center of the upper side of the lower sash locks this sash by turning through an arc of 90°.

Careful attention was necessarily given the window-operating devices, which must be capable of operation from the sides of the center bench in the large laboratories (Figure 1). The windows are sealed by double felt strips and are very tight against infiltration of air. As the windows are only slightly more than 3 feet wide, they are readily cleaned by opening one casement at a time, the mullion providing a firm hold for the cleaner.

The laboratory doors and frames (Figure 4) are also made of anodic-finished aluminum. The stiles are hollow extruded sections, 7.5 inches wide and 1.75 inches thick. There are three panels of equal size glazed with 0.25-inch glue-chipped plate glass. In the center panel of the corridor doors is a reproduction of the symbol used by alchemists to designate their laboratories. These emblems are practical as well as appropriate. They are located low enough in the door to preserve privacy, yet they permit anyone desiring entrance to

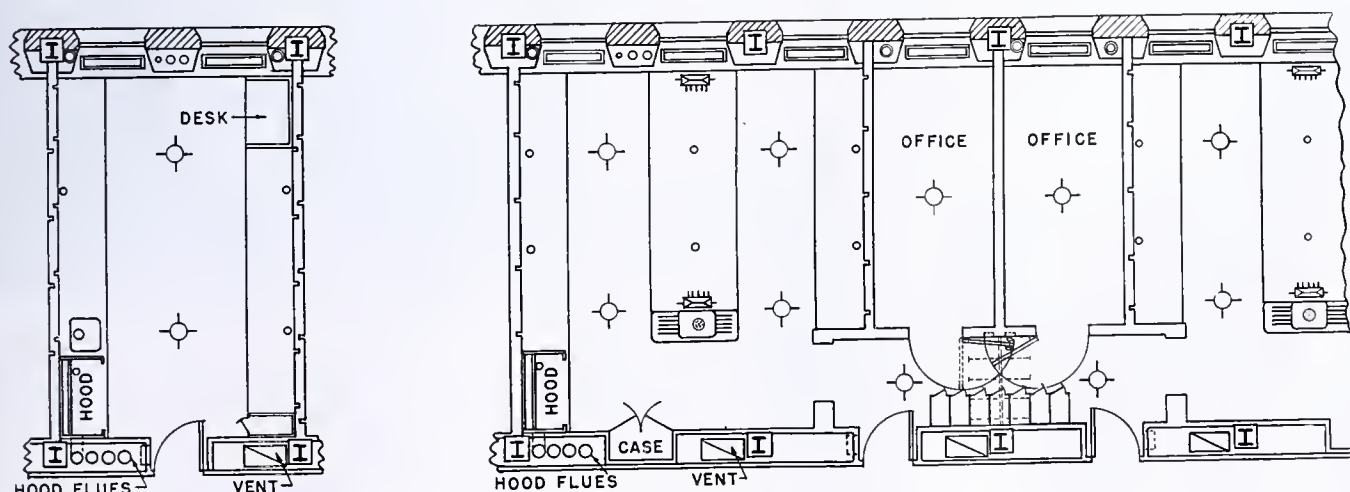


FIGURE 1. FLOOR PLAN. (Left) SMALL LABORATORY. (Right) LARGE LABORATORY





FIGURE 2. LARGE LABORATORY

determine whether work is in progress which should not be interrupted. The door butts and the exposed parts of the lock, including the knobs, are also made of aluminum.

**STRUCTURAL PROVISIONS FOR VENTILATING DUCTS AND SERVICE RISERS.** In the design of the floor slabs, slots about 15 inches wide were provided for the installation of vertical ducts and pipes in the wall between the laboratory and corridor, and in the wall at the window end of the room. Through the first-mentioned slots are carried ducts for supplying washed and filtered air to the laboratories, and also the fume-hood flues. The slots at the window ends accommodate the drain stacks, roof conductors, heating risers and returns, vertical supply pipes for water, gas, air, and vacuum, and such other supply pipes as may be necessary. At the attic floor, the corridor wall slots are sealed around the ducts and flues with concrete. The window-end slots are covered with removable steel plates, so that there can be no draft in case a panel is broken during a fire in a laboratory. If a flood occurs in the attic, water is prevented from flowing down the slot by a steel curb-angle fastened to the floor, seated in mastic. Because the hollow wall at the corridor end of the room is permanent, being made of terra cotta, the ducts enclosed therein must be composed of the most lasting materials. Armco iron, well protected inside and out with asphalt paint, was used for the fresh air ducts, and chemical stoneware for the fume-hood flues. These flues are 8 inches in internal diameter and, because of lack of space for joints of the bell-and-spigot type, the ends of the sections were ground square, and the joint was made by bolting around the pipe a metal band 2.5 inches wide and 0.25 inch thick after the ends of the pipe had been seated in mastic. Enclosed in this hollow wall are also conduits for carrying wires to the laboratory panel box at the entrance door and for the hood fan motor control.

The wall at the window end of the room consists of removable Transite panels and aluminum molding strips. Besides the vertical supply pipes, it conceals the horizontal distribution pipes to which are connected the service lines on



FIGURE 3. LABORATORY DESK

the laboratory benches. Back of these horizontal pipes, under each window, are the cast-iron convector-type radiators. The window stools, which are at laboratory bench height, are made of the same material as the bench tops. Over each radiator is a grille, V-shaped so that the heat cannot be closed off by piling books, etc., on the window stool.





FIGURE 4. DOOR, FIRE-BLANKET BOX, AND FIRE-EXTINGUISHER NICHE

Available in the attic are high-pressure steam and air which are not ordinarily supplied to the laboratory but, by the use of the floor slots and removable panels, can be brought easily to any laboratory. The attic may be reached from all floors through a large pipe shaft, and accordingly any additional service required in the future may be carried to the attic and thence to any laboratory. This feature contributes to the great flexibility of the institute's laboratory layout.

VERTICAL WALL T-SLOTS. Among the novelties developed

and first used by the institute are the vertical T-slots extending from floor to ceiling in the walls of the laboratories and in many other rooms. Figure 5 shows in cross section the shape of the slot and how it is built into the wall. The flanges of the steel wall stiffener to which the T-slot is attached by machine screws extend between the backs of the terra cotta blocks comprising a double-faced wall. The T-slot itself is an anodic-finished extruded aluminum section with 0.5-inch holes, on 1.25-inch centers in the back for supporting the shelf brackets, and having screw holes for attaching to the stiffener. Under the heads of the cadmium-plated attachment screws are fiber washers to prevent possibility of electrolysis between the steel and aluminum. The distance between T-slots is in multiples of half terra cotta blocks (8 inches) and varies from 25 to 49 inches, center to center.

Figure 5 also shows a section through a typical wall-type laboratory bench with shelf brackets, wiring trough, service lines, and drain supported by the T-slot. The laboratory bench itself is clamped to the wall by means of the T-slot. Figure 6 is a photograph of a special distillation laboratory, illustrating how the wall slots may be used to support an elaborate setup of chemical apparatus. With these slots available, it should never be necessary to drill the terra cotta to attach equipment of any kind.

PLUMBING SERVICES. Each laboratory is provided with outlets for hot, cold, and distilled water, steam, compressed air, vacuum, and gas. Copper pipe is used for hot and cold water, aluminum for distilled water, and black steel for air, vacuum, gas, and steam. The smallest size of pipe used is 0.5 inch.

On the wall benches, the service pipes are brought up from the mains under the window stools through the bench tops and carried along the walls over the benches supported by the vertical T-slots.

In the center-type benches, the pipes are carried under the tops on hangers held by the lugs on the back of the vertical bench framing members. The outlets on the center benches are in the form of anodic-finished aluminum turrets, located on the bench ends and containing electrical outlets and the services mentioned. The turret on the free end of the bench also contains the hot and cold water faucet for the double drainboard sink. The faucets for the sinks in the wall benches are supported by the service pipes above the bench top. For obvious reasons, the distilled water outlet is not placed over a sink, but directly over the bench top. Two outlets for steam are provided on the wall bench—one in the hood and one near the sink. The steam service line is carried entirely beneath the bench top, except

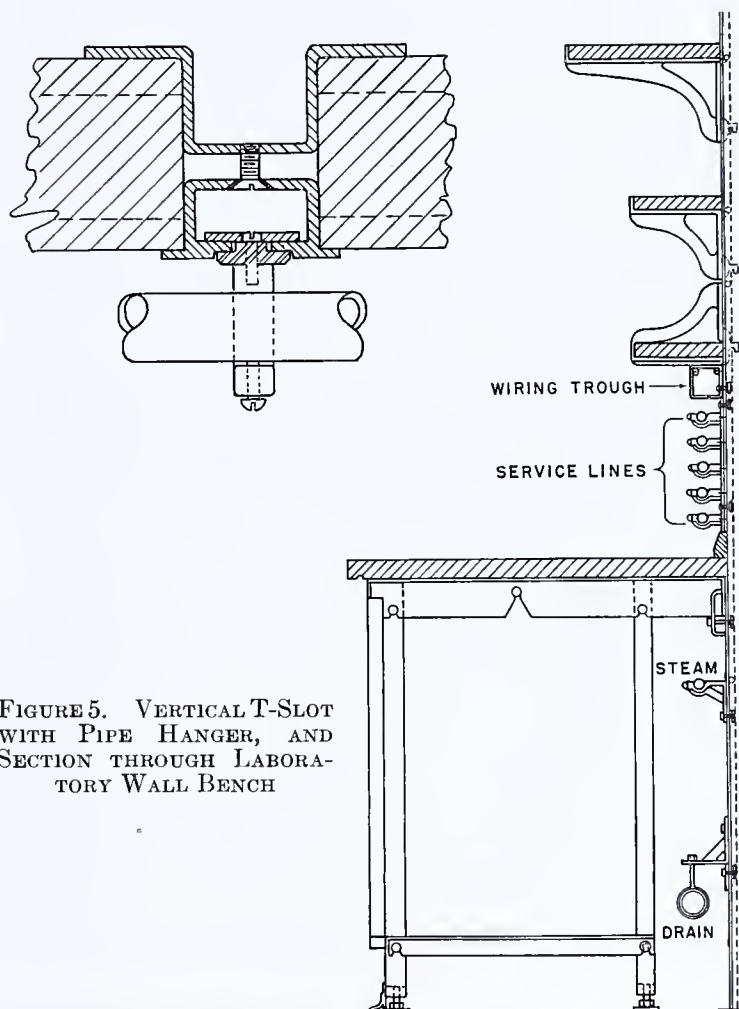


FIGURE 5. VERTICAL T-SLOT WITH PIPE HANGER, AND SECTION THROUGH LABORATORY WALL BENCH

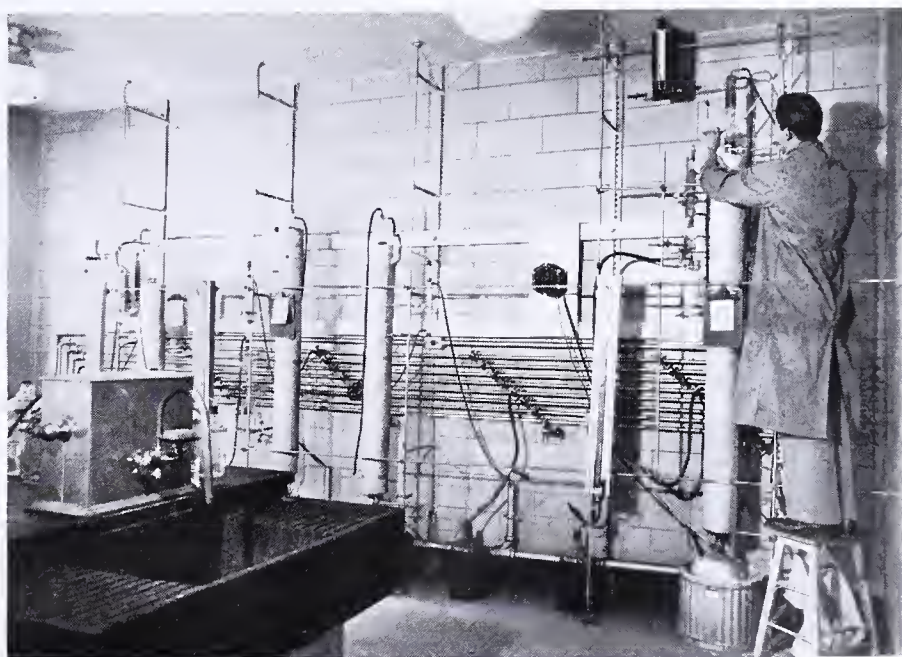


FIGURE 6. DISTILLATION LABORATORY, SHOWING UTILITY OF WALL T-SLOTS



where it is brought through the top for wall bench outlets or to the turret on the center bench. All stopcocks are of a white metal alloy, not plated, and are equipped with colored Plaskon indexes. Special combination offset elbows and unions are used at the window ends of service lines on wall benches, an arrangement conducive to easy removal for cleaning or alteration.

Drains, both vertical stacks and horizontal lines in the laboratories, are of chemical stoneware, except in a few laboratories where Karcite pipe was used. The joints are the conventional bell-and-spigot type sealed with a hot-poured asphaltic compound. A vented ceramic trap is installed for each bench at the point where the horizontal drain enters the stack. To decrease the possibility of stoppage, the stacks themselves contain no horizontal runs; they are vented through the roof. The horizontal drain lines under the first floor are made of Duriron.

The laboratory drainage system is entirely separate from the sanitary drainage system. The two systems are connected outside the building and the laboratory system is protected from sewer gas by a master trap vented to the roof.

**ELECTRICAL SYSTEM.** The distribution of alternating current is accomplished by the 3-phase 4-wire system.

There are three phase wires and a neutral; and to simplify the balancing of the permanent electrical load on the three phases, these wires have been color coded throughout—red, yellow, and black for the phase wires, and white for the neutral. Between any phase wire and the neutral, the potential is 115 volts; and as there are three phases and the voltages add vectorially at a phase angle of  $120^\circ$ , the potential between any pair of phase wires is  $115 \times \sqrt{3}$ , or 200 volts. The alternating current voltages available, then, are 115 volts single-phase (between neutral and a phase wire), 200 volts single-phase (between two phase wires), and 200 volts 3-phase (between three phase wires). The fact that the 3-phase voltage is 200 instead of the customary 220 is not a serious objection because 220-volt motors will operate satisfactorily on 200 volts, and both heating and rotating equipment designed for 200 volts is rapidly becoming available. If 220 volts must be had, suitable step-up transformers may be used; this occasional necessity for utilizing transformers is of no moment when one views the advantages of the system in general.

The circuits are brought to the standard laboratories through conduits in the hollow corridor walls. In the corridor over each laboratory door is a pull box where connections are made to the feeders for the laboratory panel box, which is located just inside the laboratory door. This panel box contains a 50-ampere main de-ion circuit breaker, a watt-hour meter, and individual de-ion circuit breakers for the lighting and laboratory bench circuits. The operating handles of the individual circuit breakers project through openings in the panel box door and therefore serve as switches as well as breakers. When a breaker trips, owing to an overload, the operating handle drops to a position intermediate between "off" and "on"; and, as soon as the cause of the overload has been removed, it is only necessary to throw the handle to the off position and then on again to restore service. The capacity of the individual circuit breakers for lighting and single-phase bench circuits is 15 amperes, and for the 3-phase bench circuit 25 amperes per phase.

From the laboratory panel box, conduits are run under the floor to the space back of the removable Transite panels at the window end of the room. From there the conduit is carried, like the plumbing service pipes, through the bench top, to wiring troughs fastened to the wall T-slots over each wall bench, and to the turrets on the center bench. The wiring trough, a new feature in the institute's equipment, consists of a formed anodic-finished aluminum trough measuring 2.5 inches square, in section, with a snap cover to close the top. Holes are provided in the front face on about 21-inch centers for receptacles installed on the inside of the trough and requiring no finish plates. A majority of the receptacles are for 115 volts single-phase, but many are connected to all four wires of the system, thus providing any of the three types of current mentioned. The wiring trough is much superior to the usual conduit and fittings, in that it is only necessary to remove the cover to find the source of any trouble arising within the trough or to make changes in the receptacles.

In addition to the receptacles in the wiring troughs and turrets, there are two single-phase and one 3-phase receptacles in the fume hood, with control switches on the outer end wall of the hood. The corridor wall of the large laboratories also contains receptacles for supplying current to equipment which cannot be conveniently plugged into the bench receptacles. Then, too, an underfloor duct is provided in the large laboratory offices to which desk lamps, etc., may be attached.

Direct or other special current may be had in each laboratory by means of a pair of wires connected to a polarized receptacle

in the wiring trough and to a plugboard in the nearest electric shaft. From the shaft plugboard, trunk lines lead to a master plugboard in the motor-generator room on the first floor. At present, direct current of 115 and 230 volts is available, but through this system every laboratory can be supplied with any type of current of which a source is provided.

**LABORATORY FURNITURE.** Owing to the variety of the institute's investigations and because the occupancy of the laboratory rooms changes from time to time as the researches expand or are replaced by new investigations, high flexibility of the laboratory equipment is of prime importance. A laboratory equipped for a study in organic chemistry can seldom be used for an investigation in, say, the field of ceramics without some change in the equipment, at least in the type of storage cabinets. While the walls are permanent, everything within the rooms is capable of easy rearrangement or entire removal. The vertical wall T-slots afford flexibility in the shelving arrangement, as well as support for additional service pipes, instruments, and apparatus which it may be desired to attach to the wall. Flexibility in the laboratory furniture has been accomplished by making the storage cabinets of uniform size so that they may be interchanged at will, and by designing the steel structure supporting the bench tops and forming the openings into which the cabinets fit so that it is composed of standardized members, most of which are used either in wall or center-type benches. These framing members are fitted firmly together without the use of bolts, screws, or nuts; the only tool required for the assembly is a rubber mallet. The bench-top slabs are likewise in sections, the joints being made without splines, and the fume hoods are so constructed that they may be easily taken into or from the laboratory.

The steel framework of the laboratory benches is composed of vertical supporting frames made of formed channels, and bottom and top horizontal or spacing frames. Riveted to the sides of the vertical frames are turned stainless-steel lugs or buttons which engage suitable slots in the horizontal frames.

The front edge of the upright frame above the level of the bottom spacer is finished with a formed pilaster which serves as a stop and division member between the removable storage cabinets. Near the top of the pilaster is welded a threaded stud to receive a clip and acorn nut for holding the storage cabinets in place. The space between the plane of the bottom spacer frame and the floor is closed by a steel sheet and aluminum cove mold set back from the face of the cabinets to allow toe room. Clips instead of bolts are used for attaching the toe-space member to the vertical frames. On the back edge of the upright frames are two additional stainless-steel lugs for attaching sway braces or pipe hangers. The two legs of each frame are provided with screws to facilitate the leveling of the bench frame structure. Identical vertical frames are employed for wall or center-type benches.

The bottom horizontal or spacer frames supporting the removable storage cabinets are constructed of formed angles welded at the corners and provided on the ends with slots to engage the lugs on the upright frames. Wall and center-type benches use the same bottom frames. The top horizontal spacer is also a four-sided angle frame with welded corners, the rear corners being reinforced with gusset plates. Provision is made on each end for engaging three lugs on the vertical frames. All spacer frames are of suitable length to make the center-to-center distance between uprights 40.75 inches. The top horizontal frames for wall benches, clamped to the wall by clips bolted to the wall T-slots, are wide enough to give a space of 6 inches for drain pipes, etc., between the back edge of the vertical frame and the wall. For center-type benches the top spacer frames are supported by two upright frames on each end, with an 8-inch space between the verticals for pipes. The service pipes for center benches are all carried below the bench top on pipe hangers engaging the lugs on the back edge of the vertical frames. Sway braces can be hooked over these rear lugs on the uprights, but are seldom necessary, as wall benches are clamped to partition walls and all benches are built out from a vertical frame attached to the wall at the window end of the room. Steel end panels, which are used on the free ends of the center benches and on shortened wall benches, are equipped with concealed slots which engage lugs on the side of the vertical frame.



Lead-coated, copper-bearing steel is used for all laboratory bench framing members. Particular attention was given to coating with lead the sheared edges of the sheets forming the framework, to prevent corrosion of the steel. Exposed surfaces of framing members are finished with baked acid-resisting aluminum paint, and the concealed parts with acid-resisting green paint.

The storage cabinets are constructed entirely of wood, except for the formed steel angle which surrounds the face of each unit and is finished with baked aluminum paint to match the exposed parts of the steel framing. The cabinets have flush fronts with concealed horizontal dividing rails and are made to such accuracy that any drawer of a given size will fit into the corresponding opening in any cabinet.

The front of the cabinet is made of 1-inch thick plywood, 7-ply, with a face of comb-grained Appalachian white oak. The cupboard doors, instead of having solid wood cores, have cores composed of cells about 1.5 inches square, which makes for lightness and decreases the tendency to warp and twist. The ends, back, top, and bottom of the cabinets are of plywood panel construction. Drawer pulls and cupboard knobs are made of black Plaskon molded in a pleasing design, which is expected to prove superior to metal because of freedom from discoloration by laboratory fumes.

Eleven types of standard size storage cabinets, which consist of various combinations of cupboards, drawers, and bins, are available. The front elevation of these units is shown in Figure 7. In addition, the smaller flat drawers are replaceable in any unit by a drawer divided into compartments for corks, etc., or by two shallow drawers for storage of pipets, thermometers, etc., as shown in the F unit. In one special laboratory two of the removable units consist of steel rubbish boxes on casters, which receive ceramic waste materials dropped into them through openings in the 0.25-inch steel bench top. Special tongs, gripping suitable cutouts in the ends of the units, make for ease in handling the standard cabinets. A specially designed four-wheel platform truck is provided for moving the units from laboratory to laboratory.

**LABORATORY SINKS AND BENCH TOPS.** All laboratory sinks are made of Karcite, a new material developed at the institute. This is a porous fired ceramic material having the voids filled with bitumen, the volatiles of which are expelled, leaving only coke or carbon. Because of the low firing temperature, the sinks are straighter than those made of a vitrified body. After firing, but before impregnation, the ceramic body is easily worked and it is thus possible to eliminate any depressions in the bottom of the sinks, so that they will drain perfectly.

Two types of sinks are used, one for mounting under the bench top and one for installation at the end of the center bench (Figure 6). The first measures 21 × 18 × 6 inches deep; while the second, which has integral double drain boards,

measures 52 × 20 inches over-all and includes a basin 24 × 18 × 8.5 inches. Each type has an integral tailpiece and a strainer made of Karcite. Cup sinks formed by extending a vertical branch of the drain pipe from the horizontal line up to a hole counterbored on the underside of the bench top are used instead of troughs for condenser discharge, etc.

Bench tops are in general of Alberene stone, 1.5 inches thick, 30 inches wide for the wall benches, and 56 inches wide for the center benches. Some benches, however, are topped with Kemite, a material similar to Karcite except that cor-dierite is used in the manufacture, thus lowering the coefficient of expansion of the material to a point where it will stand extreme local heating without fracture. Kemite was not commercially available in quantity when the building was erected. In some special laboratories, wood, stainless steel, and 0.25-inch steel plate tops are used.

**SHELVING AND SHELF BRACKETS.** By use of the adjustable shelving devised by the institute's engineers, the distance between shelves may be varied in intervals of 1.25 inches; additional shelves may be installed or the shelves may be easily removed to give wall space for instruments or to make room for bulky apparatus on the bench tops, such as large ovens or conditioning cabinets.

The shelf brackets are made of aluminum, cast in a permanent mold, and thus require no fitting. They are installed in the T-slots by placing the bracket on its side, permitting a T-lug near the top of the bracket to enter the slot, turning the bracket upright, and finally engaging a pin on the lower part of the bracket in one of the holes in the back of the T-slot. The pin is notched to hook over the back wall of the T-slot, so that the bracket cannot be dislodged by an accidental upward bump on its outer end. Die-cast shelf brackets are made for shelves both 7 and 12 inches wide, some with and some without a shelf-dividing member, so that, where desirable, shelves may overhang the last bracket and extend to the end wall of the room. The brackets for the lower shelves, which are installed directly over the wiring troughs, are of the inverted type, so that this shelf will be as low as possible. Sand-cast brackets for shelves 18 inches wide are used for analytical balance shelves on the corridor end of the large laboratories and for animal cages in some of the nutritional and pharmacologic research rooms.

The shelves in the original installation are impregnated Transite finished with an acid-resisting high-gloss lacquer, but many shelves made of wood similarly finished have since been added. During the year's experience, it has been found that the Transite shelves have a tendency to sag when heavily loaded. While this sagging can be overcome by occasionally turning the shelves, the institute plans to use in additional rooms a steel shelf with a top surface of impregnated Transite. Such a shelf will not sag, if properly designed, and will be cheaper and lighter than the Transite shelves.

Although shelves are not generally desired on the center-type laboratory benches, suitable cast-aluminum shelf supports are available. The supports are bolted to the bench tops and, as they carry no service pipes, may be erected and taken down at will. This arrangement provides two shelves, one 9 inches wide, 15 inches above the bench top, and one 7 inches wide, 9.75 inches higher (Figure 2). A lip is provided at each edge of the impregnated Transite shelves to prevent bottles from being pushed off.

**FUME HOODS.** A great deal of attention was given to fume hoods in planning the building, and several different hoods were built and tested before a design was decided upon.

The hoods adopted are of the open-front type, 54 inches long, 30 inches deep, with a clear opening in front 33 inches high. An inside height of 60 inches is provided for setting up tall apparatus and the floor of the hood is the standard laboratory bench top. Transite board is used for the construction of the hoods, the inner surfaces which come in contact with the fumes being impregnated, and the exterior finished with Vinylite paint, as on the removable panels at the window end of the room. Aluminum moldings are used for trim. A cross section of the hoods is shown in Figure 8 and an exterior view in Figure 9.

In addition to the usual draft slots at the top and floor of the hoods, an auxiliary slot about 12 inches from the bottom is incorporated, and contributes considerably to successful operation. Most gases are evolved a distance above the floor of the hood, and the pull from this slot prevents these fumes from straying out

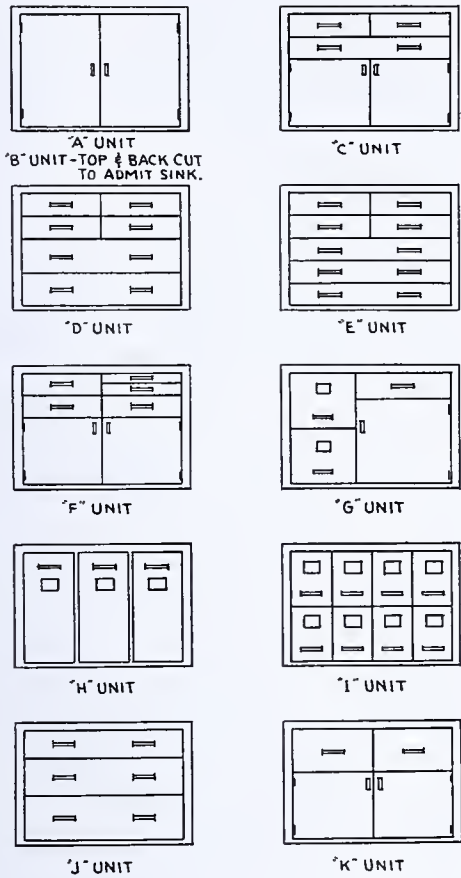


FIGURE 7. STORAGE CABINETS



of the hood. This auxiliary slot is adjustable by raising or lowering the panel beneath by means of eccentrics. Adjustment of the hood for handling light or heavy gases is made by an arrangement of slide valves in the plenum chamber, operated by a lever on the end of the hood. It is possible to apply all the draft to the top of the hood or to the bottom, to proportion it between the two in any desired ratio, or to close the draft off entirely. In the end of the plenum chamber opposite the flue is a capped opening to which may be connected a canopy installed over apparatus in the room from which it is desired to carry off fumes. The hood draft should be completely closed at such a time.

Outlets for services in the hood are all on the end opposite the flue and consist of cold water, air, gas, vacuum, steam, and the alternating currents. Cocks for controlling the plumbing services and electric switches are outside the hood. Switches are also provided for the light in the hood and for the fan motor in the attic. A cup sink for condenser discharge is located in the floor of the hood. Neon pilot lights, indicating the position of the fan motor control switch, are installed on the end of the hood and in the pull-box over the laboratory entrance door in the corridor. It is the watchman's duty on his first round at night to turn off any fans which may be running (as indicated by the pilot light in the corridor), unless a note has been placed in the label holder on the hood that the fan was intentionally left on. As a rule, each fan in the attic supplies draft for four hoods—one on each laboratory floor—but the fan will continue to run as long as any control switch is in the "on" position. Each hood is provided with a separate flue to the attic, where the four flues served by one fan are connected to a manifold constructed of steel protected with an asphalt coating. Equalization of draft to the four flues is made by dampers in the manifold. The chemical stoneware hood flue elbow projects into the laboratory about 1.5 inches and is sealed into the opening in the end of the hood plenum chamber by calking compound. As there is no duct work directly connected to the hood, the installation of a hood in or the removal from a laboratory is simplified. Suitable couplings are provided in the service piping, so that the hood can be readily disconnected.

**LABORATORY DESKS.** Although the special laboratory desks (Figure 3) were designed particularly for the small laboratories, they are also used in the offices of the large laboratories.

Their length is 43 inches, width 30 inches, and the top overhangs 5 inches at the back to clear the service pipes and drain serving the adjacent chemical bench in the small laboratories. While the single pedestal (left-hand side) of the desk includes no vertical letter-filing space, this may be had in the small laboratories by using a *G* unit (Figure 7) in the first section of the chemical bench. This unit contains two such drawers as well as a card file drawer and a stationery cupboard. Above the working surface of the desk is a bookcase section with sliding plate-glass doors and adjustable shelves.

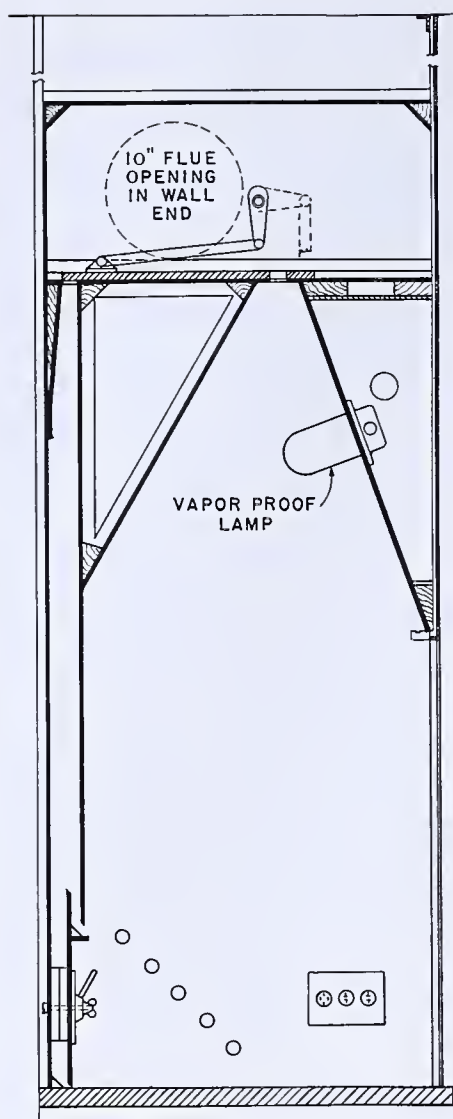


FIGURE 8. FUME HOOD

Features of the desk are a light on a flexible arm, a receptacle for attaching a microscope lamp, etc., a sliding shelf with glass insert for reference tables, a convenience tray in the knee-space drawer, a drawing board sliding in guides on the end of the desk, and removable card file sections to fit in the bookcase. The desk wiring is between receptacles on each end of the bookcase section, so that in the large laboratory offices two desks may be connected with a short cord and supplied with electricity from one outlet in the underfloor duct. No provision for the telephone is necessary, except a bushed hole in the desk top, as the instruments have the ringer box in the base. Telephone lines are brought to each laboratory and laboratory office through an underfloor duct system. The desk and bookcase unit is constructed of lead-coated steel with a baked aluminum finish and a working surface of brown linoleum.

### Special Laboratories

A special laboratory for the conditioning and testing of paper and textiles is included in the institute's facilities. In this room are maintained a temperature of  $70 \pm 2^\circ \text{F}$ . and a relative humidity of  $65 \pm 2$  per cent.

Included in the equipment for this room is a Westinghouse electrostatic precipitator, which is capable of removing from the air more than 98 per cent of the foreign matter, including the finest particles. There are also two smaller air-conditioned rooms for general use, in which the temperature can be varied from about  $40^\circ$  to  $120^\circ \text{F}$ ., and the relative humidity from 20 to 70 per cent. The temperature in these rooms can be controlled to within  $\pm 0.5^\circ \text{F}$ ., and the humidity to within  $\pm 1$  per cent or less. These rooms are insulated with cork, the paper and textile laboratory having walls of terra cotta and the other two of plaster. Wall T-slots are also available. The conditioning is accomplished by means of standard York conditioning units with forced air circulation over (1) water or brine spray cooled to approximately the dew point corresponding to the relative humidity desired, (2) a dephlegmator to remove droplets, and (3) a steam coil for re-treating the air to the desired room temperature and controlling that temperature. Steam valves are operated by controls, which start, stop, and select the speed of the compressor, and by-pass dampers are operated by air pressure from Johnson Service Company thermostats and humidistats. Freon is the refrigerant.

In a fourth air-conditioned room a temperature of  $75^\circ \text{F}$ . and a relative humidity of 65 per cent are maintained. Such studies as the measurement of volume changes in cements and the effects of high humidity in the storage of glass are carried on here. The conditioning equipment consists of a Carrier unit, including a fan, a spray, steam coils, and cooling coils supplied with chilled brine by an Audiffren refrigerating machine.

A furnace room  $25 \times 135$  feet located on the eighth floor is

used largely in connection with ceramic researches. Special features of this room include a firebrick floor, insulating firebrick flues, thermocouple conduits between central panel locations and openings in the walls, columns, and floor, and also a fresh-air supply system. The room is two stories high, there being no attic over this section of the building. Heated air from the furnaces is thus permitted to rise and escape



FIGURE 9. FUME HOOD



through the upper tier of windows. The equipment in the furnace room consists of kilns of various sizes, load test and panel spalling test furnaces for refractory brick, and pot furnaces for fusion tests and crucible heating. All these furnaces are fired with natural gas.

A small greenhouse has been built on the roof over the columns at the rear of the building. Of the four rooms in this structure, one is used for photographic work in which both still and motion picture records are made. The steam heat is controlled by a thermostat and motor-driven valve, and further temperature control is obtained in each room by means of individual thermostats and vapor motors which operate roof ventilators. Supplementary illumination, available to promote growth during winter months, is controlled by an automatic switch which turns on the electric lights twice each hour for the desired number of minutes.

Five two-window laboratory rooms on the eighth floor, without standard chemical bench equipment, are used as animal rooms for nutritional and pharmacological investigations. One room contains a steam sterilizer, 3 feet in diameter and 8 feet long, in which the cages are sterilized. The others are fitted up with either portable cage racks or shelves to support cages made with the 18-inch shelf brackets previously mentioned. The rooms also have sinks and one or two units of laboratory benches as needed.

On the second floor of the building is a suite of five rooms designed for heat-insulation research, consisting of a conductometer room, control room, general laboratory, sample preparation room, and office. The conductometer room, in which all the conductivity tests are made, is an inside room with no windows and is thus not subject to rapid changes in temperature. It adjoins the control room, to which it is connected by a system of conduits, so that the regulation of the power input to the conductometers and the recording of temperature and power data are all done in the control room. By means of a constant-voltage regulator and two tapped transformers, a regulated voltage of from 2 to 200 volts is available.

Also located on the second floor is an electric furnace room for general use in which are a Hoskins muffle furnace, a 26-kw. Hoskins heat-treating furnace, a 35-kw. high-frequency induction furnace, and other special furnaces. The Hoskins furnaces have Hoskins temperature controllers.

About 10,000 square feet of floor space on the first floor is used as a unit-plant development laboratory. Most of this space is two stories in height and is served by 5-ton electric traveling cranes. Round stoneware flues, 10 inches in diameter, and rectangular flues, 18 × 10 inches, carry off fumes and noxious gases. In addition to the regular services, 175-pound steam and 100-pound air pressures are available on this floor. By means of a hatchway and monorail crane in the receiving department on the third floor, heavy and bulky equipment can be lowered directly to the unit-plant laboratory. Electric service is provided by underfloor ducts as well as by receptacles in the walls.

A considerable part of the first floor is devoted to the chemical engineering laboratory. Here are set up, ready for use at all times, hydraulic presses, physical testing machines, dryers, centrifuges, etc. Grinding and pulverizing equipment is housed in a separate room, where provision is made for carrying off dust through the vent flues.

### Safety Features

At frequent intervals on the ceilings of the corridors on all laboratory floors are placed "fire-blanket boxes." These (Figures 4 and 10) are V-shaped metal containers, hinged to a frame attached to the ceiling and held in the closed position by a latch with a pull chain. Rolled up in the boxes are blankets tied to the frame by light cords about 2 feet long. When the latch chain is pulled, the blanket falls out and hangs in a position where a worker, who has accidentally had burning liquid spilled on his clothes, may wrap the blanket around himself and extinguish the flames. If it is necessary to take the blanket into a laboratory, the cords attaching it to the ceiling frame may be easily broken. These blankets have been used in the institute for over 15 years and have on several occasions dem-

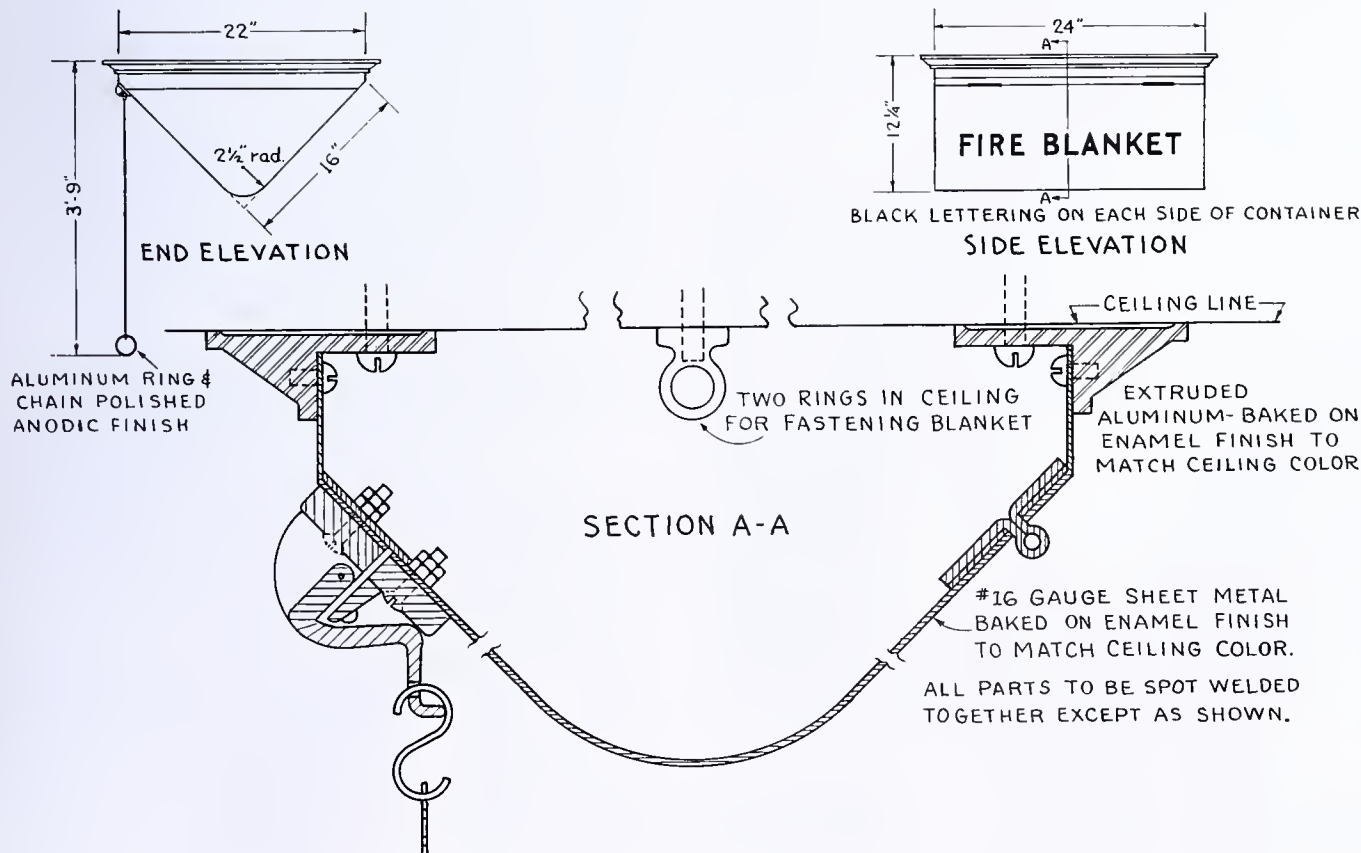


FIGURE 10. DETAIL OF THE FIRE-BLANKET BOX



onstrated their effectiveness. While shower sprays are not now used, they can be readily installed, if desired, for the water pipe is over the bench top, where a connection can be made. Recessed into the walls in all laboratory floor corridors are first-aid cabinets in which are kept the usual tape, bandages, antiseptics, and burn remedies.

Fire-extinguisher niches (Figure 4) are built into the terra cotta corridor walls in numerous places. On the laboratory floors 10-pound carbon dioxide extinguishers are placed in these niches, and 2.5-gallon foam extinguishers are used on the lower floors. Forty-gallon foam and 100-pound carbon dioxide extinguishers are located in the unit-plant section. No provision is made for combating fires with water; chemical extinguishers are much more effective in laboratories.

### Mechanical Equipment for Laboratory Services

Compressed air at 45 pounds pressure is supplied to the laboratories by two Ingersoll-Rand compressors—one class ES-1, 10 × 9 inches, and one class ER-1, 10 × 8 inches. For a limited supply of air at night a smaller compressor (class ER-1, 6 × 4 inches) is used. One hundred pound air pressure for sand blasting and other special purposes is furnished by another compressor (class ER-1, 7 × 6 inches). The thermostats controlling the heating of the building are operated by compressed air from two Gardner-Denver compressors. As the operation of the air-conditioned rooms is dependent upon the maintenance of thermostat air pressure, an alarm is arranged to ring if the pressure falls, owing to tripping of a breaker or other cause. All the air compressors have V-belt drives. The Ingersoll-Rand compressors run continuously, the air pressure being regulated by holding the intake valves closed when air is not required. Cooling water is circulated through the cylinder jackets only when air is being compressed.

A size L-3 Nash Hytor vacuum pump direct-connected to a 15-horsepower motor provides a vacuum of from 22 to 25 inches of mercury. The pump body is made of nickel-iron to withstand the effects of erosion and possible corrosion. This outfit operates intermittently.

Other mechanical equipment includes an 8-ton York refrigerating machine, using ammonia, for making ice and cooling a storage room, a York Freon machine for cooling drinking water, a 20-horsepower Spencer vacuum cleaner, a 1000-gallon steam-heated water heater, and an incinerator.

The building is heated by steam received from street lines at 175 pounds pressure. The heating steam, after being reduced in pressure, is piped up to the attic, from where it is fed downward by gravity to the radiators. Johnson Service Company's dual thermostats are used. With this system, the temperature in the building is reduced to 55° or 60° F. during nonworking hours, but any room may be brought up to daytime temperature by pressing a button on the room thermostat.

The elevator installation consists of two automatic push-button type Westinghouse passenger elevators having a speed of 500 feet per minute, an automatic service elevator, and an 8000-pound freight elevator. All elevators are automatically leveled with the landing, and on the passenger and service cars the operation of the doors is controlled by photoelectric cells. The motor-generator sets for the elevators shut down automatically if the cars are not used for a predetermined period of time and start up again when a floor button is pushed. A special electric lift near the freight elevator operates between the eighth floor and the attic—none of the elevators reach the attic (to make them do so would require penthouses on the roof, which could not be tolerated on a classical type of building). Three electric dumb-waiters with full automatic control are used. Two operate between the third and sixth floors—one between the receiving department and the main stock room, and the other between the auxiliary stock room and the main stock room. These dumb-waiters also serve the three levels of the library stack room, the shaft openings on these floors being at floor level so that book trucks can be rolled into the dumb-waiter cars. The third dumb-waiter operates between the third floor, where the receiving entrance is located, and the post office on the fourth floor, thus obviating the necessity of trucking mail on the main floor.

### Service Departments

In the main stock room, located on a mid-laboratory floor, the sixth, is maintained a large supply of chemicals, laboratory apparatus, and sundries for laboratory, office, and maintenance.

The equipment consists mostly of standard steel shelving, although special provisions have been made for storing glass tubing and rod, corks and stoppers, glass condensers, etc. Bulk solvents are kept in rectangular tanks with measuring pumps similar to those used for automobile oils. The stock is dispensed over counters in which are built glass showcases for displaying new items. Stock-room records are kept by a Kardex system, which includes perpetual inventory and purchase record cards.

On the third floor, next to the receiving department, is an auxiliary stock room which handles hardware, pipe and fittings, bar and sheet steel, lumber, etc.—materials used in the unit plants and shops, and for maintenance. It also serves as a tool room for the adjoining shop, which is reserved for the use of the research workers. Here they may repair or construct apparatus and not interfere with the mechanics in the main shop. The equipment includes a work bench, power hack saw, metal turning lathe, drill press, and grinder.

The main shop facilities comprise a completely equipped machine shop, sheet metal shop, pipe shop, wood-working shop, and electrical shop, all having skilled men. Special apparatus and mechanical equipment for various researches are constructed in these shops.

In the analytical department data are secured for research workers, relieving them of tasks for which their laboratories may not be well equipped and allowing them to devote their time to more important phases of their investigations.

There are also a glass-blowing department, a photographic and drafting department, a laboratory glassware washroom, and a laundry.

The staffs of several of the larger research projects include secretarial assistants, but most of the stenographic and typing work for the fellows is done in the general office. A vault for filing technical reports is fitted with special steel equipment, which includes flat steel boxes from which the reports may be removed by pulling the box half-way out of its place, allowing the hinged front to drop after the hinged half-top has been raised.

The library has been described in the literature. Under comfortable surroundings members of the organization have access at all times to the books and journals pertinent to their work, specialized bibliochrestic service being extended by the library staff. The library has been built up soundly around general reference and specific fellowship needs, and contains all the essential treatises on chemistry and allied sciences. It is being expanded constantly to keep abreast of research progress throughout the world and the requirements of the institute's membership.

### Literature

Publications pertaining to constructional features of the new building of Mellon Institute are as follows:

- Anonymous, *Electrical Contracting*, 36, No. 7, 7-10, 45 (1937). A description of the general wiring scheme, with construction pictures showing conduits, panel boards, etc.
- Coleman, H. S., "Planning and Equipping Laboratories for Research," *American School and University for 1933*. A description of the laboratories from the standpoint of the teacher.
- Cordrey, L. W., *Ice Refrig.*, 94, 23-4 (1938). A brief account of the equipment used for air-conditioned laboratories and for cooling drinking water, making ice, etc., in Mellon Institute.
- Hamor, W. A., "Symbolism in Mellon Institute," Pittsburgh, Pa., 1937. A sketch in booklet form of the emblemism employed in the interior of the building for ornamental purposes.
- Mellon Institute, "A Trip through Mellon Institute," Pittsburgh, Pa., 1937. A short discourse on the institute's research procedure and facilities.
- Weidlein, E. R., "Behind These Columns," Pittsburgh, Pa., 1937. A brief description of the architectural features of the building (out of print).



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Refraction, Dispersion, and Related Properties of Pure Hydrocarbons

Arranged for Use in the Analysis of Hydrocarbon Mixtures<sup>1</sup>

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IN THE technical analysis of hydrocarbon mixtures and in most phases of research on pure hydrocarbons and hydrocarbon mixtures there has long been a well recognized need for concise tables listing sound values for the physical properties of hydrocarbons of the various homologous series and for graphs showing the more important relationships that may be used in the analysis and study of hydrocarbons (25, 41, 56, 87, 125, 155, 157, 158).

This paper presents a mass of data collected by the authors over a period of years and recently revised and correlated to make the information as useful as possible. The available data for the members of the common hydrocarbon series boiling between 10° and 200° C. or slightly higher have been thoroughly combed; some data for higher boiling compounds are included, but, in this article, no attempt has been made to tabulate or evaluate data for mixed type hydrocarbons such as those covered by the excellent article of Mikeska (102).

The data tabulated are (1) boiling point at 760 mm. (or 10 mm.); (2) density  $d_4^{20}$ ; refractive index  $n_D^{20}$ ; (3) dispersion  $n_F - n_C$  and two derived constants; (4) the refractivity intercept,  $n - d/2$  (88); and (5) the specific dispersion  $(n_F - n_C)/d$  (155). These are first tabulated in detail for ten classes of hydrocarbons; tables containing averaged data for specified boiling ranges are then presented, and graphs are drawn based on these averaged properties. A few graphs are also presented showing the relationship between density and refractive index for groups of paraffin and olefin isomers.

In the tables the compounds are arranged in the order of their boiling points, and in the graphs the other properties are in general plotted against boiling point, since this arrangement is especially convenient in analytical and research work with hydrocarbon mixtures which are obtained by distillation.

A consideration of the change in density and refractive index with change in temperature is given and curves are presented showing the coefficient of cubical expansion as a function of boiling point and the change in density per degree as a function of density.

It is also shown that the introduction of the Kurtz-Ward (88) frequency coefficient into the Sellmeier-Drude equation gives

<sup>1</sup> No reprints of this article have been made. Those interested may purchase separate copies of this issue of the ANALYTICAL EDITION so long as the supply lasts from the Business Manager of the AMERICAN CHEMICAL SOCIETY, Mills Bldg., Washington, D. C. The price is fifty cents to non-members of the SOCIETY and forty cents to members.

an equation that accurately expresses the relationship between refractive index and density in the case of the excellent data of Gibson and Kincaid (57) for benzene over the temperature range of 25° to 45° C. and the pressure range of 1 to 1200 bars.

### Tabulated Data for the Physical Properties of Pure Hydrocarbons

In Tables I to X are tabulated the properties of some individual hydrocarbons representing 10 series arranged in the following order:

- Noncyclic
  - Paraffins
  - Monoolefins
  - Nonconjugated diolefins
  - Conjugated diolefins
- Monocyclic
  - Naphthenes (saturated)
  - Monoolefins
  - Conjugated diolefins
  - Aromatics
- Polycyclic
  - Dicyclic saturated
  - Tricyclic saturated

The data have been selected from the large mass of data in the literature as being the best now available, consideration being given to the reliability of the author and to the relationship between the different physical properties as a function of the constitution of the hydrocarbon.

In a limited number of cases in which there is little to choose between sets of data, two or more sets have been averaged. In a few cases in which no sound data are available, questionable values have been included and indicated. Except in rare instances, this has been done only in the case of hydrocarbons of types for which few data are available. In most instances, references to the original literature are given; otherwise reference is made to one of the recent tabulations.

In preparing these tables it was decided to tabulate boiling points to the nearest ° C. only and to correct to 760 mm. using the chart of Wilson (169), unless the pressures were very low, in which case they were corrected to 10 mm., using the chart of Nelson (108). Pressures differing by only a few millimeters from 760 were corrected with a special large-scale chart derived from Wilson's equation.



TABLE II. PHYSICAL PROPERTIES OF OLEFINS<sup>a</sup>

	Approximate Boiling Point °C.	$d_4^{20}$	$n_D^{20}$	Refractivity at 20°	Dispersion $\frac{F-C}{F-C}$	References
<b>Pentenes</b>						
2-Methylbutene (3)	20	0.6284	1.3653	1.051	...	136
Pentene (1)	30	0.6410	1.3710	1.0505	...	136
2-Methylbutene (1)	31	0.6504	1.3777	1.0525	...	136
Pentene (2), <i>cis</i>	36	0.6540	1.3817	1.0547	88	134
Pentene (2), <i>trans</i>	36	0.6486	1.3790	1.0547	...	93
2-Methylbutene (2)	38	0.6620	1.3878	1.0568	89	136
<b>Hexenes</b>						
2,2-Dimethylbutene (3)	41	0.6510	1.3759	1.0504	...	130
2-Methylpentene (4)	54	0.6646	1.3825	1.0502	83	124
3-Methylpentene (1)	54	0.6700	1.3835	1.0485	...	129
2-Methylpentene (3) (low boiling)	55	0.6702	1.3881	1.0531	...	129
2,3-Dimethylbutene (1)	56	0.6807	1.3897	1.0493	...	129
2-Methylpentene (3) (high boiling)	58	0.6709	1.3885	1.0530	...	129
2-Methylpentene (1)	62	0.6817	1.3921	1.0512	...	129
Hexene (1)	64	0.6732	1.3858	1.0492	...	129
3-Methylpentene (2) (low boiling)	66	0.6940	1.3994	1.0524	90	130
2-Ethylbutene (1)	66	0.6814	1.3990	1.0533	...	129
Hexene (3)	67	0.6816	1.3942	1.0534	...	129
2-Methylpentene (2)	67	0.6904	1.4005	1.0553	90	130
Hexene (2)	68	0.6813	1.3928	1.0521	91	132
3-Methylpentene (2) (high boiling)	68	0.6956	1.4002	1.0524	90	130
2,3-Dimethylbutene (2)	74	0.7081	1.4115	1.0575	...	129
<b>Heptenes</b>						
2,2-Dimethylpentene (4)	72	0.6827	1.3911	1.0498	...	162
2,2-Dimethylpentene (3)	76	0.6881	1.3986	1.0546	...	130
3-Ethylpentene (1)	76	0.6966	1.3971	1.0488	...	142
3,3-Dimethylpentene (1)	77	0.6961	1.3991	1.0511	...	130
2,4-Dimethylpentene (1)	81	0.6937	1.3970	1.0507	...	142
2,4-Dimethylpentene (2)	83	0.6947	1.4020	1.0547	87	125
3-Methylhexene (1)	84	0.6949	1.3970	1.0496	...	142
2,3-Dimethylpentene (1)	84	0.7054	1.4022	1.0495	...	142
2-Methylhexene (5)	85	0.6936	1.3954	1.0486	...	142
2-Methylhexene (4) (low boiling)	86	0.7020	1.3995	1.0485	...	142
3-Methylhexene (4) (low boiling)	86	0.6981	1.4000	1.0510	...	142
2,3-Dimethylpentene (3)	86	0.7126	1.4052	1.0489	...	142
2-Methylhexene (3)	87	0.6943	1.3991	1.0520	...	142
3-Methylhexene (5)	87	0.6969	1.3985	1.0501	...	142
3-Methylhexene (4) (high boiling)	88	0.7007	1.3980	1.0477	...	142
3-Methyl-2-ethylbutene (1)	89	0.7186	1.4120	1.0527	...	142
2-Methylhexene (1)	91	0.7000	1.4000	1.0500	...	142
2-Methylhexene (4) (high boiling)	91	0.6990	1.3990	1.0495	...	142
3-Methylhexene (2)	93	0.7120	1.4080	1.0518	...	142
2-Methylhexene (2)	94	0.7089	1.4075	1.0531	...	142
2-Ethylpentene (1)	94	0.7079	1.4050	1.0511	...	142
3-Ethylpentene (2)	95	0.7172	1.4120	1.0539	90	126
Heptene (1)	95	0.6993	1.3999	1.0502	86	123
Heptene (3)	96	0.7016	1.4042	1.0534	...	129
Heptene (2)	98	0.7034	1.4041	1.0524	...	129
<b>Octenes</b>						
2,2-Dimethylhexene (3)	100	0.7048	1.4068	1.0544	...	130
2,4,4-Trimethylpentene (1) (isobutylene) <sup>2</sup>	101	0.7151	1.4082	1.0507	...	149
2,4,4-Trimethylpentene (2)	102	0.7195	1.4112	1.0515	...	91
3,3-Dimethylhexene (4)	105	0.7211	1.4158	1.0543	...	149
2,3,3-Trimethylpentene (1)	106	0.7202	1.4120	1.0519	...	130
2,2,3-Trimethylpentene (3)	108	0.7363	1.4178	1.0497	...	128
2,2,3-Trimethylpentene (3)	112	0.7395	1.4232	1.0535	...	128
4-Methylheptene (3)	119	0.7318	1.4204	1.0545	90	123
2-Propylheptene (1)	119	0.7237 <sup>b</sup>	1.4170 <sup>b</sup>	1.0552	90	125
2-Methylheptene (1)	122	0.7255	1.4182	1.0555	90	124
2-Methylheptene (2)	124	0.7254	1.4169	1.0542	...	77
Octene (1) <sup>1,41</sup>	124	0.7155	1.4088	1.0516	85	119

TABLE I. PHYSICAL PROPERTIES OF PARAFFINS

	Approximate Boiling Point °C.	$d_4^{20}$	$n_D^{20}$	Refractivity at 20°	Dispersion $\frac{F-C}{F-C}$	References
<b>Pentane</b>						
2,2-Dimethylpropane	9	0.613 <sup>0</sup>	1.3513 <sup>b</sup>	...	62	100
Iso (2-methylbutane)	28	0.6197	1.3539	1.0441	63	100
Normal	36	0.6262	1.3574	1.0443	...	9, 71
<b>Hexanes</b>						
2,2-Dimethylbutane	50	0.6493	1.3690	1.0444	64	99
2,3-Dimethylbutane	58	0.6615	1.3750	1.0444	64	97
Iso (2-methylpentane)	60	0.6532	1.3715	1.0449	65	99
3-Methylpentane	63	0.6640	1.3764	1.0444	65	98
Normal	69	0.6695	1.3750	1.0452	67	101
<b>Heptanes</b>						
2,2-Dimethylpentane	79	0.6737	1.3823	1.0455	67	99
2,4-Dimethylpentane	81	0.6745	1.3823	1.0451	66	98
2,2,3-Trimethylbutane	86	0.6900	1.3894	1.0444	68	98
3,3-Dimethylpentane	90	0.6932	1.3911	1.0445	67	97
2,3-Dimethylpentane	90	0.6951	1.3920	1.0444	67	96
Iso (2-methylhexane)	92	0.6787	1.3850	1.0457	67	99
3-Methylhexane	93	0.6870	1.3887	1.0452	67	98
3-Ethylhexane	98	0.6984	1.3937	1.0445	67	96
Normal	98	0.6839	1.3878	1.0459	67	98
<b>Octanes</b>						
2,2,4-Trimethylpentane (iso-octane)	99	0.6918	1.3916	1.0457	69	100
2,2,3,3-Tetramethylbutane	107	Solid, m. p. 106.5	...	...	...	163
2,2-Dimethylhexane	107	0.6953	1.3930	1.0454	70	100
2,4-Dimethylhexane	109	0.6993	1.3952	1.0456	69	100
2,5-Dimethylhexane	110	0.7173	1.4030	1.0444	...	163
2,2,3-Trimethylpentane	112	0.7096	1.4006	1.0458	...	25
3,3-Dimethylhexane	113	0.7197	1.4045	1.0447	...	163
2,3,4-Trimethylpentane	114	0.7258	1.4074	1.0445	...	163
2-Methyl-3-ethylpentane	115	0.7123	1.4029	1.0438	72	101
2,3-Dimethylhexane	117	0.7090	1.3992	1.0447	70	99
4-Methylheptane	118	0.6980	1.3936	1.0446	70	100
Iso (2-methylheptane)	118	0.7195	1.4043	1.0456	72	101
3,4-Dimethylhexane	118	0.7274	1.4078	1.0441	...	139
3-Methyl-3-ethylpentane	119	0.7130	1.4017	1.0452	70	99
3-Ethylheptane	119	0.7051	1.3980	1.0454	...	47
Normal	125	0.7028	1.3976	1.0462	70	100
<b>Nonanes</b>						
2,2,5-Trimethylhexane	126	0.7081	1.3987	1.0447	...	76
2,3,5-Trimethylhexane	130	0.7158	1.4051	1.0472	...	60
2,6-Dimethylheptane	132	0.7129	1.4028	1.0464	...	76
2,4-Dimethylheptane	133	0.7162 <sup>a</sup>	1.4036 <sup>a</sup>	1.0455	...	35
2,5-Dimethylheptane	136	0.7145 <sup>a</sup>	1.4042	1.0470	...	35
3,3-Dimethylheptane	138	0.7304	1.4095	1.0443	...	110
3,3-Diethylpentane	139	0.7322	1.4197	1.0436	...	105
4-Ethylheptane	139	0.7407	1.4156	1.0453	71	96
2,3-Dimethylheptane	141	0.7235	1.4085	1.0467	...	60
4-Methyloctane	142	0.7245	1.4078	1.0456	72	100
2-Methyloctane	143	0.7134	1.4032	1.0465	...	159
3-Methyloctane	144	0.7210	1.4065	1.0460	...	39
Normal	150	0.7180	1.4056	1.0468	...	134
<b>Decanes</b>						
2,4,6-Trimethylheptane	144	0.7198	1.4057	1.0458	...	60
2,2,6-Trimethylheptane	152	0.7215	1.4090	1.0483	...	76
2,4-Dimethyloctane	153	0.7244	1.4090	1.0468	...	60
2,3,4-Tetramethylhexane	157	0.7547	1.4224	1.0451	...	40
3,3,5-Trimethylheptane	159	0.7562	1.4230	1.0454	...	40
2,6-Dimethyloctane	159	0.7300 <sup>a</sup>	1.4110 <sup>a</sup>	1.0465	71	97
2,7-Dimethyloctane	160	0.7244 <sup>a</sup>	1.4090 <sup>a</sup>	1.0468	72	99
3,6-Dimethyloctane	160	0.7364	1.4145	1.0463	...	156
4-Propylheptane	162	0.7360	1.4141	1.0461	72	98
4-Methylnonane	166	0.7323	1.4123	1.0461	...	32
Iso (2-methylnonane)	167	0.7242	1.4089	1.0468	72	99
5-Methylnonane	167	0.7326	1.4122	1.0459	...	160
3-Methylnonane	168	0.7335	1.4125	1.0458	72	100
Normal	174	0.7304	1.4119	1.0466	73	100
<b>Heptadecanes</b>						
2,4,7-Trimethyloctane	168	0.7331	1.4132	1.0457	...	60
2,3,7-Trimethyloctane	175	0.7566	1.4230	1.0447	...	88



2,6-Dimethylnonane Normal 5-Ethylonane	175 195 60 at 10 mm.	0.7439 0.7404 0.7507	1.4176 1.4173 1.4205	1.0456 1.0471 1.0452	74 100 ...	98 134 66	Octene (3) Octene (2)	32 at 10 mm. ...	0.7248 0.7197 <sup>b</sup>	1.4137 1.4136 <sup>b</sup>	1.0513 1.0538	87 121	...	96 47
Dodecanes							Nonenes							
2,6-Dimethyl-3-isopropyl- heptane	187	0.7655	1.432	1.0483	...	60	2,3,4-Tetramethylpentene (1)	134	0.761	1.4305	1.0500	...	163	
2-Methyl-5-propyloctane	189	0.7496	1.422	1.0472	...	60	2,5-Dimethylheptene (2)	137	0.742	1.4233	1.0523	...	160	
2,6-Dimethyldodecane	195	0.7572	1.4240	1.0454	...	60	Nonene (1)	139	0.743	...	...	...	41	
5-Propylnonane	205	0.7559	1.4258	1.0448	...	69	2,5-Dimethylheptene (3)	140	0.747	1.4250	1.0515	...	160	
Normal	216	0.7495	1.4217	1.0470	76	101	3-Ethylheptene (3)	142	0.7414 <sup>b</sup>	1.4249	1.0542	90	121	
2,3,6,7-Tetramethyloctane	75 at 10 mm.	0.7630	1.4275	1.0460	...	60	3-Methyloctene (2)	145	0.7409	1.4247	1.0542	...	164	
3-Methylhendecane	84 at 10 mm.	0.7527	1.4238	1.0465	...	60	Unknown (x)	147	0.7552	1.4286	1.0510	...	117	
Tridecanes							Nonene (2)	150	0.749	...	...	...	41	
2,5,9-Trimethyldodecane	208	0.7692	1.4297	1.0451	...	60		59 at 10 mm.	0.7302	1.4160	1.0509	...	99	
4-Propyldodecane	222	0.7609	1.4272 <sup>a</sup>	1.0468	75	98	Decenes							
5-Methyldodecane	227	0.7576	1.4244	1.0456	...	60	2-Methyl-4-ethylheptene (4)	158	0.745	1.4271	1.0546	...	41	
Normal	234	0.7571	...	...	74	97	2,7-Dimethyloctene (x)	160	0.7418	1.4255	1.0546	88	119	
5-n-Butylnonane	...	0.7615 <sup>a</sup>	1.4273 <sup>a</sup>	1.0466	...	47	4-Propylheptene (3)	161	0.7502 <sup>b</sup>	1.4291 <sup>b</sup>	1.0540	90	120	
Tetradecanes							2,6-Dimethyloctene (6)	162	0.749	1.4273	1.0528	...	163	
4,5-Di-n-propyloctane	220	0.7770	1.4334	...	...	116	Decene (1)	163	0.7530	1.4301	1.0536	90	118	
Normal	253	0.7645	...	...	...	84	2,6-Dimethyloctene (x)	164	0.7558	1.4303	1.0524	...	171	
Pentadecanes							3-Ethyoctene (2)	51 at 10 mm.	0.7545	1.4308	1.0536	...	164	
4-Methyl-6-propylhen- decane	237	0.7723	1.4325	1.0464	...	60	Decene (2)	74 at 10 mm.	0.7421	1.4217	1.0507	...	96	
6-Methyl-7-ethyldodecane	243	0.7782	1.4355	1.0464	...	60								
Unknown	244	0.7727	1.4329	1.0465	...	60	Hendecenes							
6-Propyldodecane	244	0.7720	1.4326	1.0466	...	60	1,5-Dimethylnonene (6)	167	0.7568	...	...	...	41	
2,6,10-Trimethyldodecane	248	0.7717	1.4324	1.0466	...	41	5-Methyldecene (4)	68 at 10 mm.	0.7578	1.4333	1.0544	...	164	
Unknown	264	0.779	1.4332	1.044	...	166								
Normal	271	0.7689	1.433	1.049	...	60	Dodecanes							
Hexadecanes							(Isobutylene) 3	179	0.7600	1.4306	1.0506	...	91	
7,8-Dimethyltetradecane	264	0.7788	...	...	...	60	2,6-Dimethyl-2-isopropyl- heptene (x)	188	0.7774	1.444	1.055	...	106	
Normal	288	0.7741	1.4352	1.0482	...	60	2-Methyl-5-propyloctene (x)	192	0.7609	1.434	1.0535	...	2	
4,7-Di-n-propyldecane	128 at 10 mm.	0.7841	1.4368	1.0448	...	24	2-Methylhendecene (2)	211	0.7590	1.4270	1.0475	...	28	
6,9-Dimethyltetradecane	136 at 10 mm.	0.7787	1.4348	1.0454	...	60	Dodecene (1)	214	0.758	...	...	...	41	
3-Ethyltetradecane	148 at 10 mm.	0.7789	1.4366	1.0472	77	99	2,5,8-Trimethylnonene (4)	77 at 10 mm.	0.7612	...	...	...	41	
Heptadecanes							4-Propylnonene (3)	80 at 10 mm.	0.7643	1.4362	1.0541	...	164	
Normal	303	0.7778	1.4374	1.0485	76	98	6-Methylhendecene (5)	83 at 10 mm.	0.7647	1.4368	1.0543	...	164	
Unknown	153 at 10 mm.	0.780	1.4376	1.0476	...	166								
Octadecanes							Tridecanes							
Normal	316	0.7818 <sup>b</sup>	1.4395 <sup>a</sup>	1.0486	75	96	4-Propyldecene (3)	221	0.7715	1.4391	1.0534	89	116	
3,12-Dimethyltetradecane	156 at 10 mm.	0.7924	1.4428	1.0466	...	60	5-Butylnonene (3)	85 at 10 mm.	0.7710	1.4385	1.0530	89	115	
2-Methylheptadecane	178 at 10 mm.	0.7806 <sup>a</sup>	1.4385 <sup>a</sup>	1.0486	77	99	6-Ethylhendecene (5)	97 at 10 mm.	0.7701	1.4401	1.0551	...	164	
Nonadecane														
Normal	330	0.7854 <sup>b</sup>	1.4404 <sup>b</sup>	1.0477	75	96	Tetradecenes							
Eicosane	182 at 10 mm.	0.7928 <sup>a</sup>	1.4441 <sup>a</sup>	1.0477	78	98	Tetradecene (1)	246	0.775	...	...	...	41	
3-Ethylododecane	193 at 10 mm.	0.7888 <sup>b</sup>	1.4434 <sup>b</sup>	1.0490	...	60	2-Methyltridecene (1)	116 at 10 mm.	0.7843	1.4446	1.0525	94	120	
Normal	196 at 10 mm.	0.7864 <sup>a</sup>	1.4413 <sup>a</sup>	1.0481	78	99	Tetradecene (2)	137 at 10 mm.	0.7737	1.4365	1.0501	...	96	
2-Methylnonadecane	...	0.7766	1.4356	1.0479	76	98	Hexadecenes							
Heneicosane	211 at 10 mm.	0.7968	1.4463	1.0479	...	60	Cetene	274	0.7811	1.4419	1.0514	84	108	
Docosane	...	0.7979	1.4461	1.0476	75	99	(Isobutylene) <sup>4</sup>	113 at 10 mm.	0.7944	1.4482	1.0510	...	91	
Tricosane	...	0.8054	1.4502	1.0475	...	60	3-Ethyltetradecene (2)	144 at 10 mm.	0.7917 <sup>b</sup>	1.4472 <sup>b</sup>	1.0514	88	110	
Tetracosane	...	0.8105	1.4533	1.0481	...	60	Hexadecene (2)	157 at 10 mm.	0.7830	1.4417	1.0502	...	96	
4,8,13,17-Tetramethyleico- sane	...	0.8230	1.4594	1.0479	...	141	2-Methylpentadecene (1)	...	0.8021 <sup>b</sup>	1.4466 <sup>b</sup>	1.0456	86	107	
Tricontane	...	0.8327	1.4606	1.0443	...	141	Heptadecene	161 at 10 mm.	0.778	...	...	...	...	
2,6,10,14,18,22-Hexamethyl- tetracosane	...	0.8558	1.4753	1.0474	75	96	Heptadecene (8)	...	...	...	...	...	...	
Triatriacontane	...	...	...	...	...	...								
16-Ethyltriacontane	...	...	...	...	...	...								
Pentatriacontane	...	...	...	...	...	...								
16-Butyltriacontane	...	...	...	...	...	...								
Hydrogenated rubber (C <sub>6</sub> H <sub>10</sub> ) <sub>x</sub>	...	...	...	...	...	...								

<sup>a</sup> Nomenclature. The side chain rather than the double bond is given the smallest possible number. Thus  $\text{C}-\text{C}(\text{C})=\text{C}$  is called 2-methylpentene (4) rather than 4-methylpentene (1).

<sup>b</sup> Calculated from some other temperature than 20° C.

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TABLE II. PHYSICAL PROPERTIES OF OLEFINS (Concluded)

	Approximate Boiling Point ° C.	$d_4^{20}$	$n_D^{20}$	Refractivity Intercept at 20°	Dispersion $\times 10^4$ $F-C$	References
Octadecenes						
Octadecene (1)	170 at 10 mm.	0.7898	1.4451	1.0502	..	41
2-Methylheptadecene (2)	176 at 10 mm.	0.7908 <sup>b</sup>	1.4507	1.0553	88	111
Eicosenes						
(Isobutylene) <sup>5</sup>	184 at 10 mm.	0.8176	1.4601	1.0513	..	91
3-Methylnonadecene (2)	190 at 10 mm.	0.8000 <sup>b</sup>	1.4518 <sup>b</sup>	1.0518	88	110
2-Methylnonadecene (2)	200 at 10 mm.	0.7994 <sup>b</sup>	1.4522 <sup>b</sup>	1.0525	89	109
Heneicosene	199 at 10 mm.	0.801	..	..	..	41
Tricosene	191 at 10 mm.	0.8340	1.4684	1.0514	..	91
Octacosene	219 at 10 mm.	0.8455	1.4739	1.0512	..	91
Purified rubber	...	0.9237	1.5219	1.0601	..	78

<sup>b</sup> Calculated from some other temperature than 20° C.

TABLE III. PHYSICAL PROPERTIES OF DIOLEFINS

	Approximate Boiling Point ° C.	$d_4^{20}$	$n_D^{20}$	Refractivity Intercept at 20°	Dispersion $\times 10^4$ $F-C$	References
Pentadiene						
Pentadiene (1,4)	26	0.6594	1.3880	1.0583	...	83
Pentadiene (2,3)	50	0.7023	...	...	...	86
Pentadiene (1,5)	60	0.6536	1.3919	1.0651	...	...
Hexadiene						
Hexadiene (1,5)	60	0.6903	1.4028	1.0577	100	145
Hexadiene (1,4)	64	0.6996	1.4162	1.0664	...	137
2-Methylpentadiene (2,3)	72	0.711	...	...	...	70
Heptadiene						
2,2-Dimethylpentadiene (3,4)	82	0.7183	1.4258 <sup>a</sup>	1.0675	...	49
2,4-Dimethylpentadiene (2,3)	86	0.7167 <sup>a</sup>	1.4202	1.0614	...	101
Heptadiene (1,4)	92	0.7176	1.4202	1.0614	...	137
2-Methylhexadiene (1,5)	92	0.7276 <sup>a</sup>	1.4224 <sup>a</sup>	1.0586	105	145
Heptadiene (1,2)	106	0.7306	1.4322	1.0669	...	25
Octadienes						
2,5-Dimethylhexadiene (1,5)	116	0.7466	1.4395	1.0662	...	64
Octadiene (1,5)	118	0.7314	1.4265	1.0608	...	25
3-Ethylhexadiene (2,5)	123	0.7548	...	...	...	119
Octadiene (1,4)	127	0.754	...	...	...	41
Nonadienes						
2,6-Dimethylheptadiene (1,5)	141	0.7642	1.4445	1.0624	...	65
2,6-Dimethylheptadiene (x,x)	144	0.7692	1.4460	1.0614	108	140
2,6-Dimethylheptadiene (1,x)	144	0.7628	1.4408	1.0594	109	143
Decadienes						
3,6-Dimethyloctadiene (2,6)	154	0.7767	1.4445	1.0562	...	73
2,6-Dimethyloctadiene (x,x)	163	0.7629	1.4387	1.0573	103	135
2,6-Dimethyloctadiene (2,7) <sup>b</sup>	166	0.7882	1.455	1.061	...	131
2,7-Dimethyloctadiene (2,6)	166	0.7849	1.4481	1.0557	...	73
2,6-Dimethyloctadiene (2,6)	166	0.7859	1.4490	1.0560	...	...
2,6-Dimethyloctadiene (x,x)	...	0.7736	1.4481	1.0620	108	140
2,6-Dimethyloctadiene (x,x)	52 at 10 mm.	0.7767	1.4507	1.0624	...	133

TABLE V. PHYSICAL PROPERTIES OF SATURATED CYCLICS (NAPHTHENES)

	Approximate Boiling Point ° C.	$d_4^{20}$	$n_D^{20}$	Refractivity Intercept at 20°	Dispersion $\times 10^4$ $F-C$	References
1,1-Dimethylcyclopropane	21	0.6604	1.3659	1.0357	172	61
1,2-Dimethylcyclopropane	33	0.6792 <sup>a</sup>	1.3764 <sup>a</sup>	1.0373	106	113, 176
Ethylcyclopropane	36	0.6832	1.3791	1.0375	..	123
Methylcyclobutane	36	0.6935	1.3837	1.0370	..	52
Cyclopentane	50	0.7454	1.4064	1.0337	74	139
1,1,2-Trimethylcyclopropane	53	0.6949	1.3870	1.0396	77	111
Ethylcyclobutane	72	0.7279	1.4020	1.0381	72	139
Methylcyclopentane	72	0.7472	1.4101	1.0365	96	44, 173
Cyclohexane	81	0.7781	1.4270	1.0373	78	100
1-Methyl-2-isopropylcyclopropane	81	0.7101	1.3927	1.0377	..	76
1,1-Dimethylcyclopentane	87	0.7547	1.4137	1.0366	..	34, 76
1,3-Dimethylcyclopentane	91	0.7479	1.4099	1.0360	..	41
1,2-Dimethylcyclopentane (low boiling)	92	0.7495	1.4114	1.0367	73	91
1,2-Dimethylcyclopentane (high boiling)	99	0.7718	1.4223	1.0364	74	96
Methylcyclohexane	100	0.7707	1.4243	1.0390	79	102, 44, 155
Ethylcyclopentane	101	0.7610	1.4182	1.0377	72	95
1-Methyl-1,2-diethylcyclopropane	108	0.7381	1.4102	1.0412	..	41
1-Methyl-2-isobutylcyclopropane	110	0.7402	1.4088	1.0387	..	177
1,2,3-Trimethylcyclopentane	113	0.7565	1.4165	1.0374	74	98
1,2,4-Trimethylcyclopentane	114	0.7595	1.4194	1.0397	75	99
1,1,2-Trimethylcyclopentane	114	0.7713	1.4226	1.0370	75	97
Cycloheptane	119	0.8099	1.4440	1.0391	..	123
1,4-Dimethylcyclohexane (trans)	119	0.7655	1.4205	1.0378	75	98
1,3-Dimethylcyclohexane (trans)	119	0.762	1.4248	1.0358	77	101
1,3-Dimethylcyclohexane (cis)	121	0.7735	1.4259	1.0392	77	100
1,4-Dimethylcyclohexane (cis)	121	0.7671	1.4226	1.0391	77	100
1,3-Diethylcyclohexane	122	0.7973	1.4388	1.0402	..	175
1,1-Dimethylcyclohexane	123	0.7809 <sup>a</sup>	1.4305	1.0401	78	100
1,4-Diethylcyclohexane	123	0.7800	1.4294	1.0394	..	34
1,2-Dimethylcyclohexane (trans)	123	0.800	1.4415	1.0415	77	100
1,2-Dimethylcyclohexane (cis)	124	0.7760	1.4270	1.0390	76	98
Isopropylcyclopentane	127	0.7963	1.4360	1.0379	76	103
Propylcyclopentane	129	0.7717	1.4248	1.0394	75	97
Ethylcyclohexane	130	0.7718	1.4250	1.0391	75	97
1,1,2,3-Tetramethylcyclopentane	130	0.7840	1.4324	1.0404	76	97
1-Methyl-4-isopropyl-2-isobutylcyclohexane	133	0.7763 <sup>a</sup>	1.4271 <sup>a</sup>	1.0380	77	100
1,3-Trimethylcyclohexane (cis)	133	0.8265	1.4565	1.0433	..	132
1,3-Trimethyl-2-ethylcyclopentane	138	0.7930	1.4367	1.0402	..	44
1,3,5-Trimethylcyclohexane (trans)	138	0.7756	1.4274	1.0396	75	97
1,2,4-Trimethylcyclohexane (trans)	139	0.7720	1.4270	1.0410	77	100
1,2,5-Trimethylcyclohexane (cis)	140	0.7813	1.4311	1.0405	77	99
1,3,5-Trimethylcyclohexane (cis)	140	0.7742	1.4299	1.0419	78	101
1-Methyl-3-isopropylcyclopentane	142	0.7759	1.4299	1.0415	77	100
1,2,4-Trimethylcyclohexane (cis)	142	0.7754 <sup>a</sup>	1.4271 <sup>a</sup>	1.0394	76	98
1-Methyl-2-isopropylcyclopentane	142	0.7850	1.4333	1.0408	78	99
1,2,3-Trimethylcyclohexane (trans)	143	0.7792	1.4279	1.0383	77	99
1,2,3-Trimethylcyclohexane (cis)	143	0.7914	1.4357	1.0400	78	99
1,1,2-Trimethyl-3-isopropylcyclobutane	146	0.7930	1.4367	1.0402	79	99
Isobutylcyclopentane	146	0.7598	1.4200	1.0401	75	99
1,3-Methylcyclohexane	149	0.7795	1.4294	1.0397	78	100
Cyclooctane	150	0.814	1.4487	1.0417	..	138
1-Methyl-2,3-diisopropylcyclopentane	151	0.839	1.4586	1.0391	..	168
1,4-Methylcyclohexane	151	0.779	1.4305	1.0410	..	59
1,1-Diethylcyclopentane	151	0.8027	1.4388	1.0375	..	138
1,2-Methylcyclohexane	153	0.803	1.4400	1.0385	..	138
Isopropylcyclohexane	153	0.7902	1.4363	1.0412	77	99
n-Propylcyclohexane	156	0.7898	1.4358	1.0409	78	99
1,2-Dimethyl-3,4-diethylcyclobutane	156	0.7729	1.4248	1.0384	76	98



1,2-Diisopropylcyclobutane	158	0.7755	1.4279	1.0402	...	90
1,2-Dimethyl-3-isopropylcyclopentane	160	0.7885	1.4329	1.0387	...	41
1,2,3,5-Tetramethylcyclohexane (trans)	163	0.8140	1.4465	1.0395	77	95
1-Methyl-2,5-diethylcyclopentane	164	0.7839	1.4308	1.0398	76	97
1,2,4,5-Tetramethylcyclohexane (trans)	167	0.8100	1.4444	1.0394	77	97
1-Methyl-4-isopropylcyclohexane	168	0.7962	1.4375	1.0394	78	98
1,2,3,5-Tetramethylcyclohexane (cis)	169	0.8166	1.4484	1.0401	85	104
Isobutylcyclohexane	170	0.7950	1.4389	1.0414	78	98
tert-Butylcyclohexane	170	0.811	1.4464	1.0409	...	158
1-Methyl-2-isopropylcyclohexane	171	0.8142	1.447	1.040	...	...
1,2,4,5-Tetramethylcyclohexane (cis)	171	0.8122	1.4462	1.0401	83	102
1,3-Methyl-n-propylcyclohexane	172	0.794	1.4377	1.0407	...	158
1,2-Methyl-n-propylcyclohexane	176	0.808	1.4445	1.0405	...	158
1,4-Methyl-n-propylcyclohexane	176	0.796	1.4393	1.0413	...	158
1,2,5-Trimethylcyclohexane	178	0.7944	1.4361	1.0389	77	97
1,2,3-Triethylcyclopentane	178	0.7955	1.4365	1.0387	77	97
sec-Butylcyclohexane	179	0.809	1.4458	1.0413	...	158
n-Butylcyclohexane	180	0.797	1.4408	1.0423	...	158
Isobutylcyclohexane	194	0.798	1.4420	1.0430	...	158
tert-Butylcyclohexane	194	0.8196	1.4520	1.0422	...	158
1,3-Methyl-n-butylcyclohexane	195	0.801	1.4418	1.0413	...	158
1,4-Methyl-n-butylcyclohexane	196	0.805	1.4415	1.0390	...	158
1,2-Methyl-n-butylcyclohexane	197	0.811	1.4467	1.0412	...	158
n-Butylcyclohexane	202	0.802	1.4428	1.0418	...	158
1,2-Methyl-n-amylicyclohexane	218	0.814	1.4487	1.0417	...	158
n-Octylcyclopentane	112 at 10 mm.	0.8142	1.4475	1.0404	...	174

<sup>a</sup> Value calculated from some temperature other than 20° C.

TABLE VI. UNSATURATED CYCLES

	Approximate Boiling Point °C.	d <sub>20</sub> <sup>o</sup>	n <sub>D</sub> <sup>20</sup>	Refractivity at 20°	Dispersion $\frac{F-C}{F-C} \times 10^4$	References
1-Methylcyclobutene (1)	38	0.7105 <sup>a</sup>	1.4052 <sup>a</sup>	1.0500	...	53
Cyclopentene	44	0.7742 <sup>a</sup>	1.4230 <sup>a</sup>	1.0359	...	73
1-Methylcyclopentene (3)	73	0.772	...	...	...	41
1-Methylcyclopentene (1)	73	0.7757	...	...	...	98
1,1-Dimethylcyclopentene (2)	79	0.7579	1.4190	1.0405	...	74
Cyclohexene	83	0.8101	1.4465	1.0415	97	119
1,2-Dimethylcyclopentene (1)	97	0.7831	1.4348	1.0433	...	34
1,2-Dimethylcyclopentene (2)	103	0.794	1.442	1.047	...	41
1-Methylcyclohexene (3)	103	0.7985	...	...	...	41
1-Methylcyclohexene (2)	105	0.805	...	...	...	41
1,2-Dimethylcyclopentene (5)	105	0.7952	1.4442	1.0466	...	34
1-Ethylcyclopentene (2)	108	0.796	1.443	1.045	...	41
1-Ethylcyclopentene (1)	109	0.7974	1.4426	1.0439	...	41
1,1,2-Trimethylcyclopentene (2)	109	0.7827 <sup>a</sup>	1.4331 <sup>a</sup>	1.0417	...	47
1-Methylcyclohexene (1)	111	0.8103 <sup>a</sup>	1.4497	1.0446	...	10
Cycloheptene	114	0.8228	1.4552	1.0438	...	124
1,1-Dimethylcyclohexene (3)	120	0.8028 <sup>a</sup>	1.4442 <sup>a</sup>	1.0428	93	116
1,1-Dimethylcyclohexene (1)	121	0.8024	1.443	1.042	...	41
1,2,3-Trimethylcyclohexene (1)	121	0.7970 <sup>a</sup>	1.4445 <sup>a</sup>	1.0460	...	47
3,4-Dimethylcyclohexene (1)	124	0.807	1.444	1.041	...	41
3,5-Dimethylcyclohexene (1)	124	0.801	1.444	1.044	...	41
1,2-Dimethylcyclohexene (3 and 4)	125	0.8064	1.4454	1.0422	92	114

<sup>a</sup> Calculated from some other temperature than 20° C.

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TABLE IV. CONJUGATED DIOLEFINS

	Approximate Boiling Point °C.	d <sub>20</sub> <sup>o</sup>	n <sub>D</sub> <sup>20</sup>	Refractivity at 20°	Dispersion $\frac{F-C}{F-C} \times 10^4$	References
Pentadienes						
2-Methylpentadiene (1,3)	34	0.6805	1.4216	1.0814	155	225
(isoprene)	43	0.6815 <sup>a</sup>	1.4309 <sup>a</sup>	1.0902	166	243
Pentadiene (1,3) (piperylene)						17, 48
Hexadienes						
2,3-Dimethylbutadiene (1,3) <sup>b</sup>	70	0.7261	1.4394	1.0763	145	200
Hexadiene (1,3)	73	0.7152	1.4418	1.0840	...	25
2-Methylpentadiene (2,4)	76	0.7193	1.4520	1.0934	163	226
2-Methylpentadiene (1,3)	76	0.7196	1.4467	1.0869	162	226
Hexadiene (2,4) (low boiling)	76	0.7108	1.4427	1.0873	158	222
3-Methylpentadiene (1,3)	78	0.7279	1.4511	1.0877	164	225
Hexadiene (2,4) (high boiling)	79	0.7152	1.4493	1.0907	166	232
Hexadiene (2,5)	80	0.7205	1.4514	1.0912	...	...
Heptadienes						
2,3-Dimethylpentadiene (1,3) <sup>b</sup>	93	0.7432	1.4428	1.0712	155	208
2,4-Dimethylpentadiene (1,3) <sup>b</sup>	93	0.7368	1.4405	1.0721	...	...
3-Methylhexadiene (1,3)	102	0.7448 <sup>a</sup>	1.4550 <sup>a</sup>	1.0826	...	...
2-Methylhexadiene (2,4)	104	0.7439	1.4611	1.0893	168	226
Heptadiene (2,4)	105	0.7340	1.4494	1.0814	159	214
3-Methylhexadiene (2,4)	108	0.7585	1.4591	1.0799	...	...
Octadienes						
2,4-Dimethylhexadiene (2,4) <sup>b</sup>	115	0.7607	1.4530	1.0727	...	...
2-Methylheptadiene (3,5)	117	0.7323	1.4505	1.0844	151	206
2,5-Dimethylheptadiene (1,3) <sup>b</sup>	117	0.7412	1.4502	1.0796	...	...
4-Methylheptadiene (2,4)	132	0.7590	1.4645	1.0850	151	200
3,4-Dimethylhexadiene (2,4) <sup>b</sup>	133	0.7825	1.4652	1.0740	...	...
3-Methylheptadiene (2,4)	134	0.7625	1.4623	1.0811	...	...
Nonadienes						
2,6-Dimethylheptadiene (2,4)	141	0.7481	1.4571	1.0783	...	...
2,6-Dimethylheptadiene (1,3) <sup>b</sup>	141	0.7567	1.4571	1.0783	...	...
3,5-Dimethylheptadiene (2,4) <sup>b</sup>	145	0.7692	1.4604	1.0758	...	...
7-Methyloctadiene (2,4)	149	0.7501	1.4553	1.0803	148	197
2-Methyloctadiene (4,6) <sup>b</sup>	149	0.7505	1.4533	1.0780	...	...
4-Methyloctadiene (3,5)	150	0.7679	1.4652	1.0812	157	204
Decadienes						
2,5-Dimethyloctadiene (3,5) <sup>b</sup>	165	0.7792	1.4637	1.0741	...	...
2,6-Dimethyloctadiene (4,6) <sup>b</sup>	166	0.7790	1.4640	1.0745	...	...
2,6-Dimethyloctadiene (x,x)	52 at 10 mm.	0.7767	1.4607	0.0724	...	...
Heptadecadienes						
2,6-Dimethylnonadiene (4,6) <sup>b</sup>	165	0.7817	1.4632	1.0724	...	...

<sup>a</sup> Calculated from some temperature other than 20° C.

<sup>b</sup> Best data available, but questionable.



TABLE VI. UNSATURATED CYCLICS (Concluded)

	Approximate Boiling Point ° C.	$d_4^{20}$	$n_D^{20}$	Refractivity Intercept at 20°	Dispersion $\times 10^4$ $\frac{F-C}{F-C}$	References
1,3-Dimethylcyclohexene (3)	125	0.8021 <sup>a</sup>	1.4440 <sup>a</sup>	1.0430	95	119
1,3-Dimethylcyclohexene (1)	125	0.8006	1.4487	1.0484	...	41
1,3-Dimethylcyclohexene (4)	127	0.8020	1.4470	1.0480	98	122
1,3-Dimethylcyclohexene (5)	127	0.7970 <sup>a</sup>	1.4437 <sup>a</sup>	1.0452	95	119
1,4-Dimethylcyclohexene (1)	127	0.8004 <sup>a</sup>	1.4446	1.0444	94	117
2,4-Dimethylcyclohexene (x)	127	0.804	1.4480	1.0462	...	158
1,5-Dimethylcyclohexene (1)	127	0.8031	1.4476	1.0460	...	41
1-Isopropylcyclopentene (1)	132	0.8141	1.4506	1.0436	...	100
1,1,2,3-Tetramethylcyclopentene (2)	134	0.8034	1.4441	1.0424	...	145
1-Ethylcyclohexene (1)	136	0.8308 <sup>a</sup>	1.4620	1.0466	97	117
1,2-Dimethylcyclohexene (1)	136	0.8264 <sup>a</sup>	1.4586 <sup>a</sup>	1.0454	100	121
1-Methylcycloheptene (1)	138	0.824	1.4578	1.046	...	152
1,1,3-Trimethylcyclohexene (2 and 3)	138	0.8070 <sup>a</sup>	1.4448 <sup>a</sup>	1.0413	97	118
1,1,2-Trimethylcyclohexene (4)	139	0.8218	1.4561	1.0452	...	15
1-Methyl-3-isopropylcyclopentene (2)	139	0.789	1.4369	1.0424	...	14
1,3-Dimethyl-2-ethylcyclopentene (1)	140	0.8032 <sup>a</sup>	1.4488 <sup>a</sup>	1.0472	97	120
1,4-Trimethylcyclohexene (3)	140	0.8051 <sup>a</sup>	1.4460 <sup>a</sup>	1.0435	97	117
1,3,5-Trimethylcyclohexene (x)	140	0.7983 <sup>a</sup>	1.4459 <sup>a</sup>	1.0438	97	121
1,1-Diethylcyclopentene (2)	144	0.8082	1.4469	1.0438	75	117
1,2,5-Trimethylcyclohexene (4)	145	0.8045	1.4479	1.0456	94	117
1,4,5-Trimethylcyclohexene (1)	145	0.805	1.448	1.045	...	3, 4
Cyclooctene	145	0.835	1.474	1.046	...	41
1,1,2-Trimethylcyclohexene (2)	149	0.8238	1.4562	1.0444	96	117
1-Methyl-3-ethylcyclohexene (x)	150	0.8132	1.4536	1.0470	94	117
1,2,3-Trimethylcyclohexene (1)	150	0.8271 <sup>a</sup>	1.4593 <sup>a</sup>	1.0458	99	120
1-Ethyl-4-methylcyclohexene (x)	151	0.812	1.4528	1.0468	...	138
1,2-Diethylcyclopentene (x)	152	0.8091	1.4510	1.0465	94	116
2-Ethyl-4-methylcyclohexene (x)	152	0.813	1.4544	1.0479	...	78
1-Isopropylcyclohexene (x)	153	0.828	1.4594	1.0454	...	138
1-Methyl-4-ethylcyclohexene (3)	154	0.8138	1.4519	1.0450	...	15 av.
1-Isopropylcyclohexene (1)	156	0.8263	1.4593	1.0462	96	116
1-n-Propylcyclohexene (x)	156	0.824	1.4578	1.0458	...	138
1-Ethyl-2-methylcyclohexene (x)	157	0.830	1.4630	1.048	...	138
1-Methyl-2,5-diethylcyclopentene (1)	164	0.8113 <sup>a</sup>	1.4523 <sup>a</sup>	1.0467	97	119
1,2,4,5-Tetramethylcyclohexene (1)	166	0.8169 <sup>a</sup>	1.4564 <sup>a</sup>	1.0485	98	120
1,1,2,3-Tetramethylcyclohexene (3)	168	0.8289	1.4625	1.0480	...	4
1-Methyl-4-isopropylcyclohexene (3)	169	0.8130 <sup>a</sup>	1.4543 <sup>a</sup>	1.0478	94	116
1-n-Propyl-4-methylcyclohexene (x)	173	0.813	1.4533	1.0468	...	47, 156
2-n-Propyl-4-methylcyclohexene (x)	173	0.814	1.4546	1.0476	...	138
1-Methyl-4-isopropylcyclohexene (1)	176	0.8230 <sup>a</sup>	1.4554 <sup>a</sup>	1.0439	...	138
1-n-Propyl-2-methylcyclohexene (x)	177	0.830	1.4627	1.0477	...	150
1-n-Butylcyclohexene (x)	182	0.826	1.4591	1.0461	...	138
1,2,5-Triethylcyclopentene (1)	182	0.813 <sup>a</sup>	1.4533 <sup>a</sup>	1.0468	94	116
2-Isobutyl-4-methylcyclohexene (x)	185	0.810	1.4530	1.0480	...	47 av.
2-n-Butyl-4-methylcyclohexene (x)	195	0.818	1.4574	1.0484	...	138
1-Isobutyl-4-methylcyclohexene (x)	195	0.824	1.4596	1.0476	...	138
1-n-Butyl-4-methylcyclohexene (x)	197	0.816	1.4558	1.0478	...	138
1-n-Butyl-2-methylcyclohexene (x)	198	0.831	1.4637	1.0482	...	138
1-n-Amylcyclohexene (x)	204	0.829	1.4605	1.0460	...	138
1-n-Amyl-2-methylcyclohexene (x)	219	0.832	1.4646	1.0486	...	138
1,3,4-Trimethyl-1-isopropylcyclohexene (3)	78 at 10 mm.	0.8388 <sup>a</sup>	1.4644	1.0450	94	112
Cyclorubber	...	0.989	1.5385	1.0425	...	121

<sup>a</sup> Calculated from some other temperature than 20° C.

TABLE VIII. PHYSICAL CONSTANTS OF AROMATICS (Concluded)

	Approximate Boiling Point ° C.	$d_4^{20}$	$n_D^{20}$	Refractivity Intercept at 20°	Dispersion $\times 10^4$ $\frac{F-C}{F-C}$	References
1,3-Dimethyl-5-ethylbenzene	185	0.861	1.5013 <sup>a</sup>	1.0612	...	172
1,4-Dimethyl-2-ethylbenzene	185	0.8802 <sup>a</sup>	1.5015 <sup>a</sup>	1.0644	...	80
1,5-Dimethyl-2-ethylbenzene	186	0.8742 <sup>a</sup>	1.5015 <sup>a</sup>	1.0644	...	80
<i>neo</i> -Pentylbenzene	186	0.8565	1.4876	1.0594	...	43
(1,1-Diethyl)-toluene	187	0.8717	1.4969	1.0616	...	80
1,2-Dimethyl-4-ethylbenzene	188	0.8739	1.5027	1.0658	...	30, 70
(3-Dimethyl)-butylbenzene	188	0.8642	1.4953	1.0632	...	43
3,4-Dimethyl-1-ethylbenzene	189	0.8704	1.4947 <sup>a</sup>	1.0613	139	161
<i>tert</i> -Amylbenzene	190	0.8668 <sup>a</sup>	1.4924	1.0616	...	58, 80
1-Methyl-4- <i>tert</i> -butylbenzene	190	0.8616	1.4924	1.0616	...	7
<i>sec</i> -Amylbenzene	193	0.8614	1.4906	1.0599	...	113
1,2,3,5-Tetramethylbenzene (isodurene)	195	0.8584	1.4873	1.0581	...	43
1-Ethyl-4-isopropylbenzene	196	0.8906	1.5104	1.0651	...	43
1-Methyl-4- <i>sec</i> -butylbenzene	197	0.8576 <sup>a</sup>	1.4910 <sup>a</sup>	1.0622	...	80
1-Methyl-3- <i>n</i> -butylbenzene	197	0.8632	1.4912	1.0596	...	3
1-Methyl-4- <i>n</i> -butylbenzene	198	0.8612 <sup>a</sup>	1.4924 <sup>a</sup>	1.0618	140	163
1-Methyl-3,5-diethylbenzene	198	0.8636	1.4940	1.0622	...	43
1-Methyl-2- <i>n</i> -butylbenzene	199	0.8790	1.4957	1.0612	...	109
1,2-Dimethyl-4-isopropylbenzene	200	0.8690 <sup>a</sup>	1.4980 <sup>a</sup>	1.0627	143	164
1-Methyl-3,5-diethylbenzene	200	0.879	1.4884	1.0593	...	41
<i>n</i> -Amylbenzene	201	0.8582	1.4954	1.0633	151	175
1,2-Dimethyl-4-propylbenzene	202	0.8642	1.4954	1.0633	...	18
1-Ethyl-4-propylbenzene	203	0.866 <sup>a</sup>	1.5185	1.0678	157	174
1,2,3,4-Tetramethylbenzene (1,1,1-Methyl-4-propyl)-toluene	204	0.9014 <sup>a</sup>	1.4955	1.0588	...	43
1,3-Dimethyl-4-propylbenzene	205	0.8734	1.5005	1.0611	...	43
1-Methyl-3-(2,2-dimethyl-propyl)-benzene	208	0.8673	1.4912	1.0620	...	41
1,4-Disopropylbenzene	208	0.8585	1.4912	1.0620	...	112
1-Methyl-4-isopropylbenzene	210	0.8629	1.4950	1.0635	...	21
1,3,5-Trimethyl-2-ethylbenzene	211	0.8858	1.5111	1.0682	154	174
1,2,5-Trimethyl-4-ethylbenzene	211	0.8835 <sup>a</sup>	1.5086 <sup>a</sup>	1.0649	151	171
1-Propyl-4-isopropylbenzene	213	0.859	1.4943	1.0648	...	43
1-Methyl-2-ethyl-4-isopropylbenzene	214	0.8674	1.4944	1.0607	139	160
1-Methyl-5-ethyl-2-propylbenzene	214	0.8762	1.4938 <sup>a</sup>	1.0631	154	179
1,3,5-Trimethylbenzene	217	0.8614 <sup>a</sup>	1.4950	1.0663	...	43
1-Methyl, 3,5-diisopropylbenzene	217	0.8668	1.4950	1.0616	...	155
$\pi$ , $\pi$ -Triethylbenzene	217	0.8655	1.4990	1.0663	...	43
(2,3-Dimethyl)butylbenzene	217	0.8721	1.4970 <sup>a</sup>	1.0572	...	80
1,2,4-Triethylbenzene	218	0.8797 <sup>a</sup>	1.490	1.059	...	26
<i>n</i> -Hexylbenzene	220	0.8613	1.5033	1.0647	...	43
1,3,5-Trimethyl-2- <i>n</i> -propylbenzene	221	0.8775	1.5030	1.0646	...	43
1-Butyl-4-isopropylbenzene	222	0.8610	1.4930	1.0623	...	43
1,2,4-Trimethyl-5-isopropylbenzene	223	0.8803	1.5070	1.0658	...	43
1-Methyl- $\pi$ , $\pi$ -diisopropylbenzene	93 at 10 mm.	0.8670	1.4900	1.0665	...	43
1-Methyl-2-propyl-4-isopropylbenzene	225	0.8650 <sup>a</sup>	1.4937 <sup>a</sup>	1.0612	135	156
1,2,4-Trimethyl-5- <i>n</i> -propylbenzene	226	0.887	1.5095	1.0665	...	43
1,1,1-Triethyltoluene	226	0.8675	1.4945	1.0607	...	43
1-Methyl-2,6-diisopropylbenzene	228	0.8768	1.5030	1.0646	...	43
<i>tert</i> -Butyl- <i>m</i> -cymene	228	0.8660	1.4950	1.0620	...	43
1-Methyl-3-ethyl-6-isobutylbenzene	229	0.8795	1.4972	1.0653	...	43
$\pi$ - <i>tert</i> -Butyl- <i>p</i> -cymene	230	0.8788	1.4972	1.0653	...	43
1,3,5-Trimethyl-2-isobutylbenzene	230	0.8767 <sup>a</sup>	1.4995 <sup>a</sup>	1.0606	143	164
1-Methyl-2-isobutyl-4-isopropylbenzene	230	0.9137	...	...	...	43
Dimethylisoamylbenzene	233	0.8867	...	...	...	43
1-Methyl-2-butyl-4-isopropylbenzene	235	0.8897	...	...	...	43



TABLE VII. PHYSICAL PROPERTIES OF UNSATURATED CYCLICS WITH TWO CONJUGATED DOUBLE BONDS

	Approximate Boiling Point ° C.	d <sub>4</sub> <sup>20°</sup>	n <sub>D</sub> <sup>20°</sup>	Refractivity at 20°	Dispersion $\frac{F-C}{F-C}$	References
Cyclopentadiene	40	0.8026 <sup>a</sup>	1.4429 <sup>a</sup>	1.0416	132	164
Cyclohexadiene (1,3)	80	0.8405	1.4750	1.0548	...	6, 8, 47
1-Methylcyclohexadiene (2,4)	101	0.8273 <sup>a</sup>	1.4674 <sup>a</sup>	1.0537	...	63, 165
5,5-Dimethylcyclohexadiene (1,3)	111	0.8113 <sup>a</sup>	1.4996 <sup>a</sup>	1.0666	...	20
Cycloheptadiene (1,3)	121	0.8660 <sup>a</sup>	1.4996 <sup>a</sup>	1.0666	160	185
1,5-Dimethylcyclohexadiene (1,3)	127	0.821	1.471	1.061	...	41
1,2-Dimethylcyclohexadiene (2,6)	136	0.8521	1.4895	1.0632	...	20
1,3-Dimethylcyclohexadiene (1,3)	136	0.8373	1.4856	1.0670	...	71, 118
1,4-Dimethylcyclohexadiene (1,3)	136	0.8330 <sup>a</sup>	1.4800 <sup>a</sup>	1.0635	...	5, 11, 126
1-Methyl-4-ethylcyclohexadiene (1,3)	161	0.8379 <sup>a</sup>	1.4823 <sup>a</sup>	1.0634	...	5, 11, 126
1-Methyl-4-isopropylcyclohexadiene (1,3)	176	0.8350 <sup>a</sup>	1.4785 <sup>a</sup>	1.0610	...	9, 11, 114

<sup>a</sup> Value calculated from some temperature other than 20° C.

TABLE VIII. PHYSICAL CONSTANTS OF AROMATICS

	Approximate Boiling Point ° C.	d <sub>4</sub> <sup>20°</sup>	n <sub>D</sub> <sup>20°</sup>	Refractivity at 20°	Dispersion $\frac{F-C}{F-C}$	References
Benzene	80	0.8788	1.5012	1.0618	166	189
Toluene	111	0.8670	1.4969	1.0633	160	185
Ethylbenzene	136	0.8669	1.4959	1.0624	153	176
p-Xylene	138	0.8610 <sup>a</sup>	1.4961 <sup>a</sup>	1.0656	158	183
m-Xylene	139	0.8641	1.4974	1.0654	158	183
o-Xylene	144	0.8811	1.5055	1.0650	159	181
Isopropylbenzene (cumene)	153	0.8620 <sup>a</sup>	1.4922 <sup>a</sup>	1.0612	148	172
Propylbenzene	159	0.8618	1.4920	1.0611	145	168
m-Methylstyrene	162	0.8673 <sup>a</sup>	1.4975 <sup>a</sup>	1.0639	153	177
p-Methylstyrene	162	0.8619 <sup>a</sup>	1.4943 <sup>a</sup>	1.0634	150	174
o-Methylstyrene	165	0.8807 <sup>a</sup>	1.5041 <sup>a</sup>	1.0638	155	170
1,3,5-Trimethylbenzene (mesitylene)	165	0.8653	1.4990 <sup>a</sup>	1.0663	154	179
tert-Butylbenzene	169	0.8669	1.4925	1.0591	...	43
1,2,4-Trimethylbenzene (pseudocumene)	169	0.8762 <sup>a</sup>	1.5048 <sup>a</sup>	1.0667	150	171
Isobutylbenzene	170	0.8664 <sup>a</sup>	1.4926 <sup>a</sup>	1.0594	140	161
sec-Butylbenzene	171	0.8623	1.4901	1.0589	146	167
1-Methyl-2-tert-butylbenzene (o-cymene)	174	0.8623	1.4901	1.0589	146	167
1-Methyl-2-isopropylbenzene (m-cymene)	175	0.8759 <sup>a</sup>	1.5003 <sup>a</sup>	1.0624	...	167
1-Methyl-3-isopropylbenzene (p-cymene)	176	0.8605 <sup>a</sup>	1.4925 <sup>a</sup>	1.0623	144	167
1-Methyl-4-isopropylbenzene (hemimellitene)	177	0.8569	1.4906	1.0622	144	168
1,2,3-Trimethylbenzene (mesitylene)	176	0.8951	1.5139 <sup>a</sup>	1.0664	157	176
1,2-Diethylbenzene (xylene)	177	0.8811	1.5036	1.0630	148	168
1,3-Diethylbenzene	181	0.8617 <sup>a</sup>	1.4955 <sup>a</sup>	1.0647	146	169
1-Methyl-3-propylbenzene	182	0.8625 <sup>a</sup>	1.4951 <sup>a</sup>	1.0639	146	169
n-Butylbenzene	183	0.8606	1.4936	1.0633	148	171
1-Methyl-4-propylbenzene	183	0.8606 <sup>a</sup>	1.4954 <sup>a</sup>	1.0651	137	159
1,4-Diethylbenzene	183	0.8649 <sup>a</sup>	1.4973 <sup>a</sup>	1.0649	145	166
1-Methyl-2-propylbenzene	184	0.8737 <sup>a</sup>	1.4995 <sup>a</sup>	1.0627	...	...

<sup>a</sup> Calculated from some other temperature than 20° C.

TABLE IX. DICYCLIC SATURATED HYDROCARBONS

	Approximate Boiling Point ° C.	d <sub>4</sub> <sup>20°</sup>	n <sub>D</sub> <sup>20°</sup>	Refractivity at 20°	Dispersion $\frac{F-C}{F-C}$	References
3,3-Dimethyl-dicyclo-(0,1,3)-hexane	115	0.8043	1.4021	1.0337	...	20
Saturated dicyclic C <sub>8</sub> H <sub>16</sub>	132	0.7972	1.4346	1.0360	79	99
Dicyclo-(0,x,x)-octane	140	0.8604	1.4615	1.0313	...	20
2,6,6-Trimethyldicyclo-(0,1,3)-heptane	141	0.8223	1.4465	1.0355	...	20
2,2-Dimethyldicyclo-(1,2,2)-heptane (camphenilene)	143	0.8546	1.4555	1.0282	...	20
1,3,3-Trimethyldicyclo-(1,2,2)-heptane (fenchene)	149	0.8316	1.4462	1.0304	...	20
6,6-Dimethyldicyclo-(1,1,3)-heptane (nopinane)	149	0.8630	1.4641	1.0326	...	20
2,3-Dimethyldicyclo-(1,2,2)-heptane (santane)	151	0.8700	1.4630	1.0280	...	41
4-Methyl-1-isopropylidicyclo-(0,1,3)-hexane (sabinene)	157	0.8163	1.4393	1.0312	...	20
Methylfenchene	161	0.8521	1.4526	1.0366	82	93
Dicyclononane	163	0.8784	1.4705	1.0313	...	47
2,7,7-Trimethyldicyclo-(1,2,3)-heptane (isobornylene)	164	0.8579	1.4590	1.0300	...	20
2,6,6-Trimethyldicyclo-(1,1,3)-heptane (pinane), trans	165	0.8501	1.4585	1.0335	...	41
2,6,6-Trimethyldicyclo-(1,1,3)-heptane (pinane), cis	168	0.8562	1.4624	1.0343	...	41
3,7,7-Trimethyldicyclo-(0,1,4)-heptane (carane)	170	0.8410	1.4562	1.0362	...	41
1-Methyldicyclo-(1,3,3)-nonane	178	0.8416	1.4529	1.0321	...	20
Decahydronaphthalene, trans	185	0.8699	1.4697	1.0329	...	20
Decahydronaphthalene (mixed isomers)	192	0.8895	1.4765	1.0318	88	95
Decahydronaphthalene, cis	194	0.8963	1.4811	1.0329	...	20
Dicyclopentylmethane	207	0.8568	1.4642	1.0360	...	20
9-Methyl-3-isopropylidicyclo-(1,3,3)-nonane	233	0.8643	1.4660	1.0338	85	97
Dicyclohexylmethane	252	0.8763	1.4771	1.0390	...	47

TABLE X. TRICYCLIC SATURATED HYDROCARBONS

	Approximate Boiling Point ° C.	d <sub>4</sub> <sup>20°</sup>	n <sub>D</sub> <sup>20°</sup>	Refractivity at 20°	Dispersion $\frac{F-C}{F-C}$	References
2,2,5-Trimethyl-3,6-methylenedicyclo-(0,1,3)-hexane (cyclofenchene)	145	0.8600	1.4522	1.0222	87	101
Northcycloekasontalane	184	0.885	1.4686	1.0261	...	41
Dodecahydrofluorene	253	0.9190	1.485	1.026	...	20
Tricyclodecane	...	0.9500	1.4958	1.0208	...	20



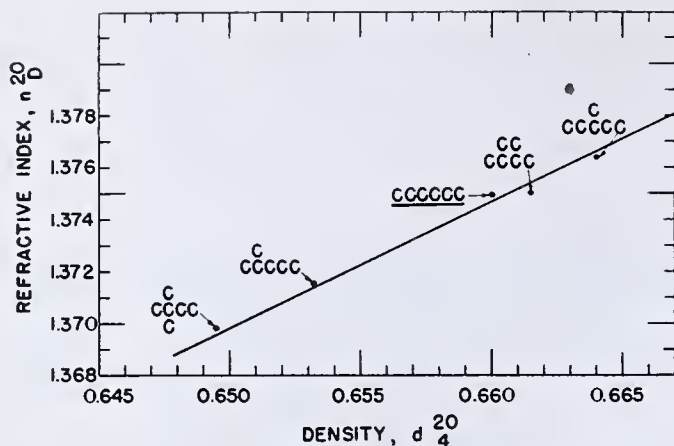


FIGURE 1. REFRACTIVE INDEX AND DENSITY OF ISOMERIC HEXANES

Densities and refractive indices are tabulated as  $d_4^{20}$  and  $n_D^{20}$ . It is the well considered opinion (156) of the authors that  $20^\circ\text{C}$ . should be adhered to as the standard reference temperature for recording and tabulating refractive index and density data for both high and low molecular weight hydrocarbons which are liquid at  $20^\circ\text{C}$ . As is well known, some investigators still report densities and indices at different temperatures and much of the older work was reported at the most diverse temperatures. In the case of the old style tabulations such as Landolt-Börnstein (89) and the Annual Tables of Physical Constants (97) the compilers, lacking an adequate basis for correction, were compelled to tabulate data at whatever temperatures were in the original literature. This made correlation almost impossible. For the more common hydrocarbons, temperature coefficients are becoming known. This has permitted the more recent compilations, such as those in the International Critical Tables (69) and the Science of Petroleum (41) and the unusually complete tabulations of Egloff and von Grosse (43, 60), to give data at  $20^\circ\text{C}$ . At best, data converted to  $20^\circ\text{C}$ . are substitutes for values actually determined at the standard temperature. Therefore, it is to be hoped that all workers in the field of hydrocarbon research will adopt this reference temperature. In the case of high-melting compounds it is suggested that  $80^\circ\text{C}$ . be adopted as a secondary reference temperature since very few hydrocarbons melting above  $80^\circ\text{C}$ . are encountered, and since  $80^\circ\text{C}$ . has been used both by Ferris and co-workers (51) and by Katz (72).

Dispersions are given for the  $F - C$  (or  $H_\beta - H_\alpha$ ) interval. The refractive index for the  $C$  or  $H_\alpha$  line and the  $F$  or  $H_\beta$  line may be obtained by the following equations based on the Cauchy formula:

$$n_C^{20} = n_D^{20} - 0.292 (n_F - n_C) \quad (1)$$

$$n_F^{20} = n_D^{20} + 0.708 (n_F - n_C) \quad (2)$$

Except in a few cases the dispersion data tabulated are from the same reference as given for the density and refractive index data; therefore separate literature references have not been given for any dispersion data. If it be desired to convert the  $F - C$  dispersion to dispersion for any other spectrum interval  $X - Z$ , then one may use the equation

$$(n_X - n_Z) = (n_F - n_C) \frac{(1/\lambda_X^2 - 1/\lambda_Z^2)}{1.9095}$$

Values for the wave length  $\lambda$  and  $1/\lambda^2$  for the common spectral lines are given in Table XI.

In addition to boiling point, density, refractive index, and dispersion, two derived constants are tabulated—namely, the refractivity intercept  $n - d/2$  of Kurtz and Ward (88) and the specific dispersion  $(F - C)/d$  (155). The refractivity intercept is extremely useful in many problems relating to hydro-

carbon analysis and identification. For example, the low values of the refractivity intercepts for the naphthenes are especially helpful in showing the presence of such compounds in hydrocarbon mixtures. Again, it may frequently be used for the quantitative analysis of hydrocarbon mixtures either as a part of a scheme of analysis such as described by Kurtz and Headington (87) for complex mixtures or alone for simpler mixtures, such, for example, as a mixture of conjugated and nonconjugated diolefins or of aromatics and naphthenes. The specific dispersion is also very valuable, since it is practically constant for all saturated hydrocarbons whether cyclic or noncyclic and is useful in determining aromatics.

TABLE XI. EXTRAPOLATION AND INTERPOLATION OF REFRACTIVE INDICES

Spectrum Line	Wave Length $\lambda$ Å.	$\frac{1}{\lambda^2} \times 10^{-8}$
$C$ or $H_\alpha$	6563	2.322
$D_1$	5896	2.877
$D$	5893	2.880
$D_2$	5890	2.883
$H_e f$	5876	2.900
Hg green	5461	3.353
$H_e v$	5016	3.975
$F$ or $H_\beta$	4861	4.231
$H_e c$	4713	4.502
$H_e i$	4472	5.000
$g$ (Hg blue)	4358	5.265
$G'$ or $H$	4341	5.307

Graphs of refractivity intercept versus boiling point give peaks at those boiling points where mono- or diolefins or aromatics predominate and troughs at those boiling points where naphthenes predominate. If both naphthenes and aromatics are present in the same cut, the presence of the latter can be shown by the high specific dispersion.

### Relationship between Structure and Physical Properties of Hydrocarbon Isomers

It is a tribute to the skill and patience of organic chemists that such a mass of data as is summarized in Tables I to X can be collected. Years ago, the late T. W. Richards (122) was interested in correlating such data, but was hampered by the lack of accurate values for a sufficient number of hydrocarbons, by the existing state of the art on the synthesis of hydrocarbons and, in particular, by the lack of established generalizations that now permit sifting data to reject values that are obviously out of line and to select those that must be at least reasonably accurate. For example, it is clear now that the physical properties of many of the octanes synthesized for Richards by Clarke (35) were not reliable. Recent data by Boord (25), Maman (96), Smittenberg, Hoog, and Henkes (139), and Whitmore and Laughlin (163) confirm for the octanes generalizations that have been drawn from other work for the isomers of the lower members of the series. Such generalizations show the inadequacy of the older octane data. The point is illustrated by a comparison of the data for two of the isomers, the average refractivity intercept for seventeen octanes being 1.0452.

Isomer	$d_4^{20}$	$n_D^{20}$	Refractivity Intercept	Reference
2,3-Dimethylhexane	0.7206	1.4098	1.0495	35
	0.7123	1.4013	1.0451	139
2,2,3-Trimethylpentane	0.7173	1.4187	1.0601	35
	0.7173	1.4030	1.0444	163

The high value of the refractivity intercept of many of Clarke's octanes indicates either the presence of olefins or incorrect refractive index data.

Since the paraffins are the simplest series, a study of the effect of structure on the physical properties of isomers should begin there. The papers of Morgan, Carter, and Duck (105)



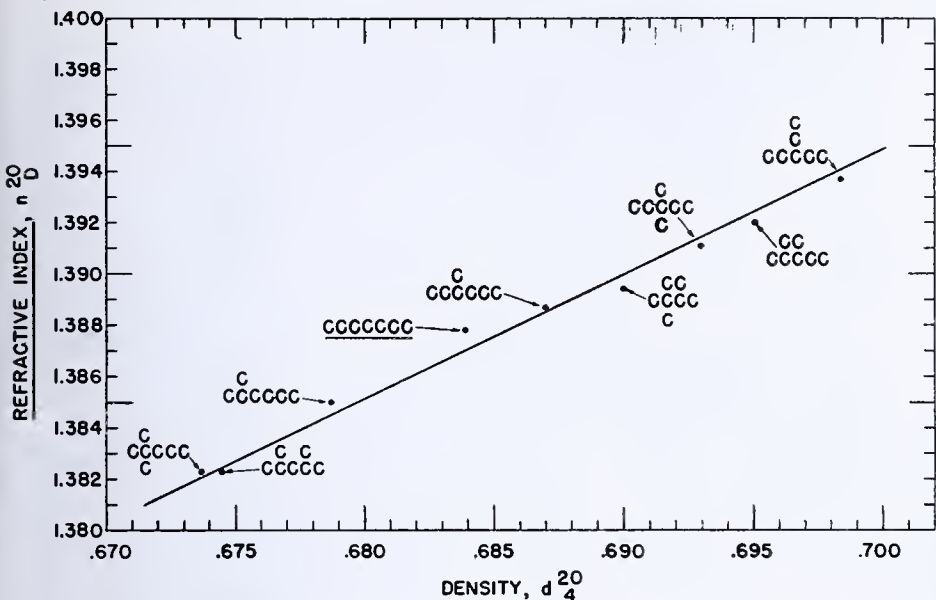


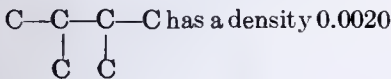
FIGURE 2. REFRACTIVE INDEX AND DENSITY OF ISOMERIC HEPTANES

in 1925 and of Edgar and Calingaert (42) in 1930 placed the study of isomeric paraffins on a relatively sound basis; in fact, a careful consideration of the data of the latter authors for the isomeric heptanes leads to the writers' conclusion (88) that the classic Newton specific refraction equation,  $\frac{n^2 - 1}{d}$ , accurately represents the relationship between  $n$  and  $d$  for hydrocarbon isomers.

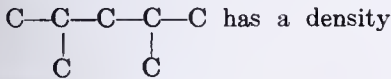
Figures 1, 2, and 3 show the data in the present tabulation for the isomeric hexanes, heptanes, and octanes, the carbon skeleton being indicated and a straight-line curve corresponding to the average Newton specific refraction equation being shown. The close agreement between the experimental data and the curves for the Newton equation is obvious. Graphs for the isomeric nonanes and decanes are similar to those presented.

Among other things, the graphs also strikingly illustrate some of the generalizations of Morgan, Carter, and Duck (105), Edgar and Calingaert (42), and Boord (25). It is clear that substitution that tends to increase the symmetry of the molecule raises the density and index, whereas substitution that tends to make the molecule less compact, decreases both  $d$  and  $n$ .

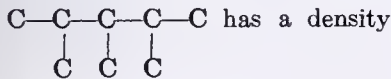
The very large effect of symmetry, or central grouping, is shown not merely by the fact that a perfectly symmetrical hydrocarbon such as 3,3-diethylpentane has a density of 0.0342 higher than that of normal nonane but also by many other comparisons. Thus



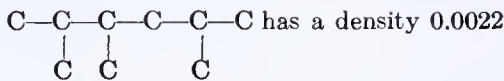
higher than that of the normal isomer, but



0.0094 lower than that of the normal isomer. Again

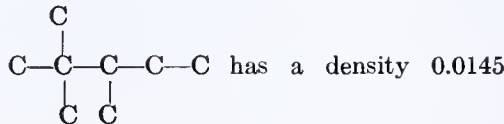


0.0169 higher than that of the normal isomer, but

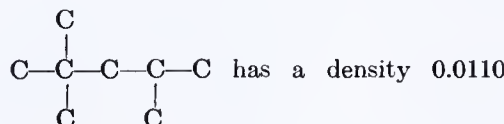


lower than the normal isomer.

Similarly



higher than that of the normal isomer, but



lower than that of the normal isomer.

The relationships are expressed numerically in Table XII. Edgar and Calingaert (42) stated, "It would appear probable, therefore, that approximate values of most of the physical properties of paraffin hydrocarbons can be predicted with reasonable assurance when their structure is known." The steady increase in sound data available now makes it possible to test this statement. For the 6 paraffins from  $C_5$  to  $C_{10}$ , the effect of substitution in the 2 position is to lower the density in comparison to the normal isomer by an average of 0.0056 with an average deviation of 0.0007. The average increase in density (in comparison to the normal isomer) by substitution in the 3 position for the five paraffins is 0.0032 with a mean deviation of 0.0005. The degree of approximation of the predictable properties is rapidly approaching the accuracy with which these properties are determined in many laboratories.

It is beyond the scope of the present paper adequately to discuss the effect of structure on the physical properties of isomeric olefins. Figure 4, the data for which are largely from the excellent work of Soday and Boord (142), shows the values for the isomeric heptenes, the curve again corresponding to the Newton equation. Naturally, the conflicting effects of the position of the double bonds and the substituted

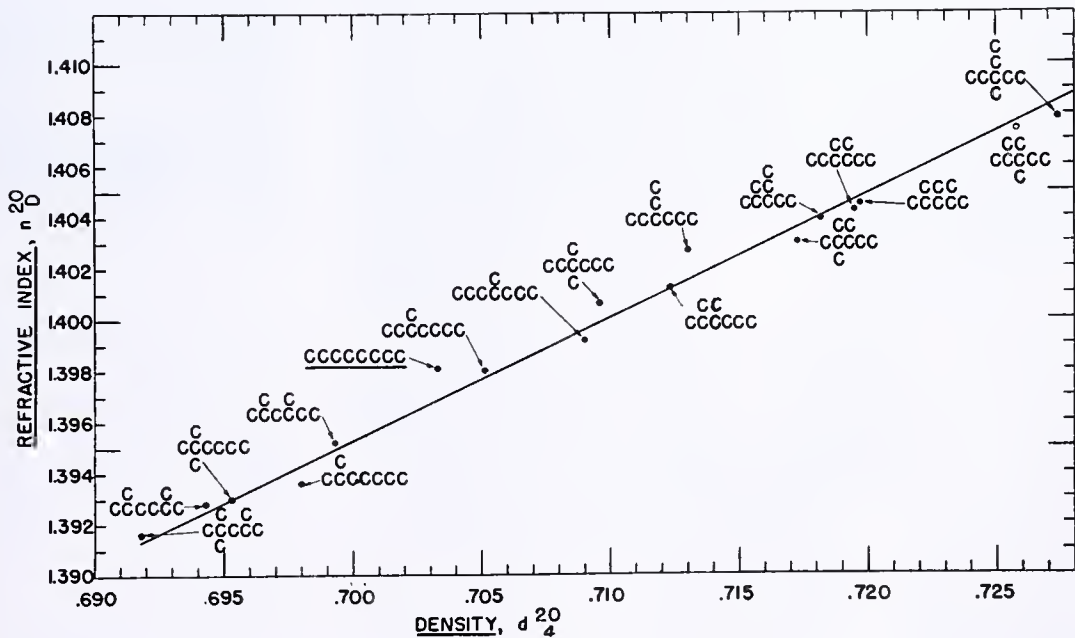


FIGURE 3. REFRACTIVE INDEX AND DENSITY OF ISOMERIC OCTANES



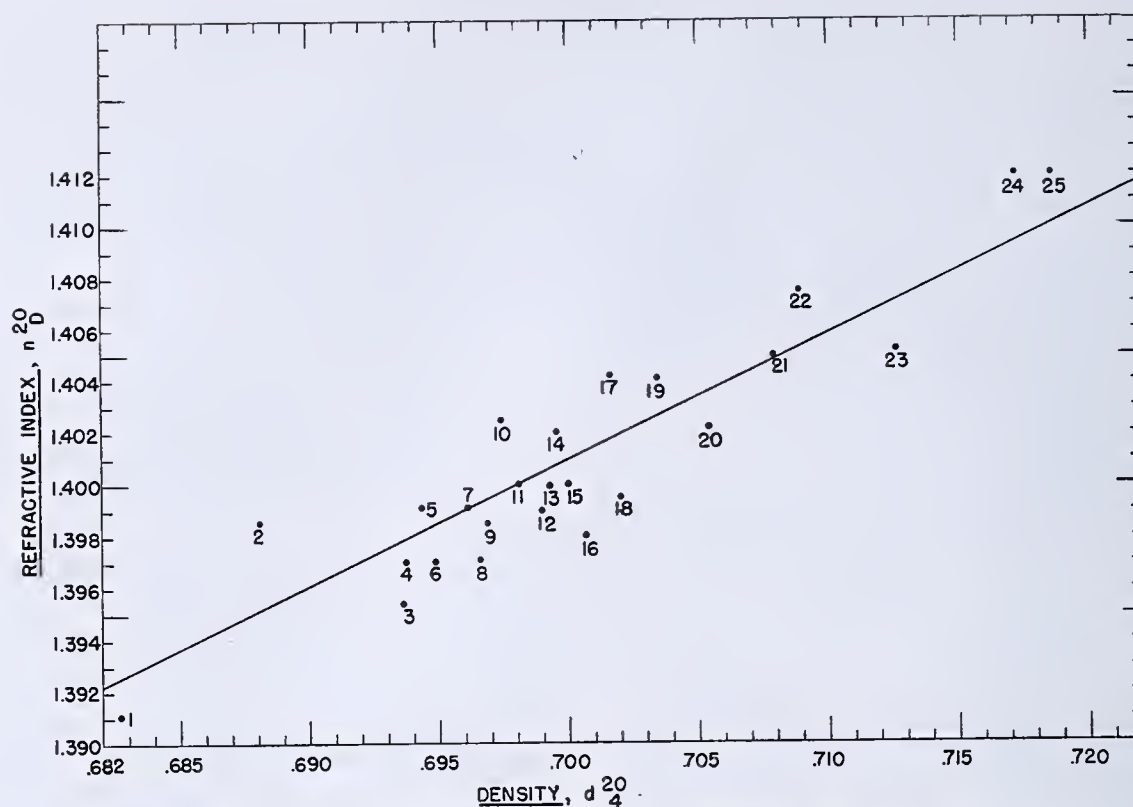
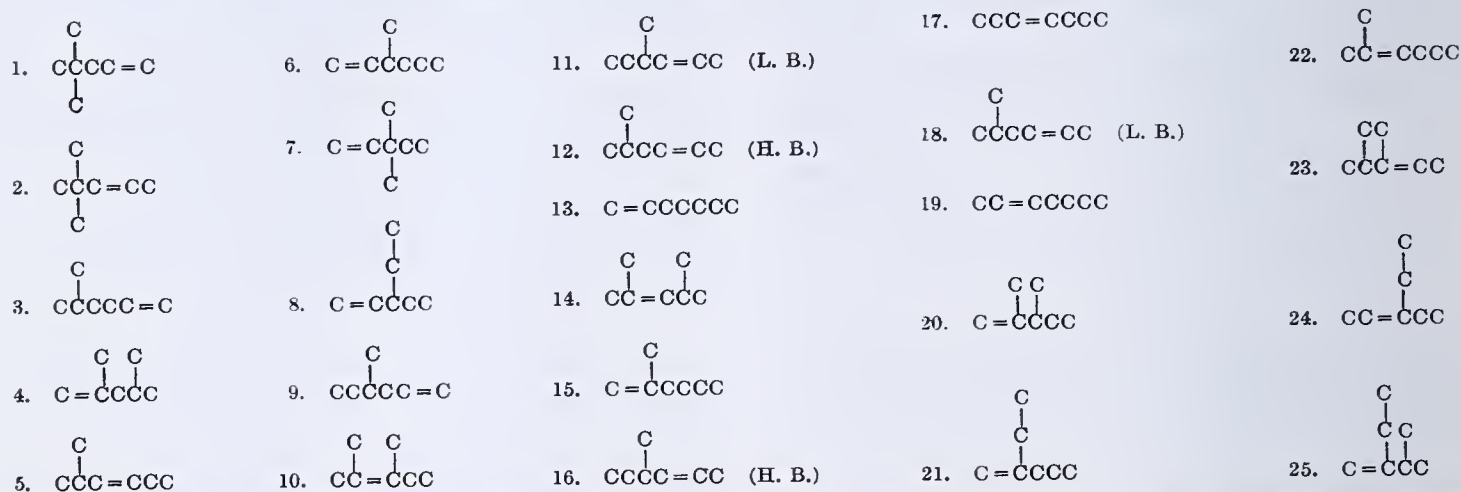


FIGURE 4. REFRACTIVE INDEX AND DENSITY OF ISOMERIC HEPTENES STRUCTURE CORRESPONDING TO NUMBERED POINTS IN FIGURE 4



carbon atoms result in more scattering than in the case of the paraffins.

The subject has been discussed by Schmitt and Boord (129) and more recently by Boord (25) who called attention to some important generalizations, including the effect of structure on boiling point. Their work should be consulted by anyone interested in the subject.

One of the most important effects is that of substitution of

alkyl groups for the hydrogen attached to the unsaturated carbon of an olefin. This raises the physical constants rather sharply.

The following comparisons are interesting in showing the increases as a result of a shift in the position of the substituted group either from the same position at the opposite end of the chain or from an adjacent carbon atom to the unsaturated carbon:

Structure	$d_4^{20^\circ}$	$\Delta$	Structure	$d_4^{20^\circ}$	$\Delta$
$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	0.6936	.....	$\begin{array}{c} \text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	0.6994 <sup>a</sup>	.....
$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	0.7000	+0.0064	$\begin{array}{c} \text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	0.7120	+0.0126
$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	0.6966	.....	$\begin{array}{c} \text{C}=\text{O}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	0.6966	.....
$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	0.7079	+0.0113	$\begin{array}{c} \text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	0.7172	0.0206

<sup>a</sup> Average of high-boiling and low-boiling isomers.



TABLE XII. EFFECT OF SUBSTITUTION ON DENSITY OF PARAFFINS

(Densities of branched isomers compared to density of normal paraffin  $\times 10^4$ )

Position	Substitution	Group	C <sub>5</sub> Pentanes	C <sub>6</sub> Hexanes	C <sub>7</sub> Heptanes	C <sub>8</sub> Octanes	C <sub>9</sub> Nonanes	C <sub>10</sub> Decanes
2	Methyl		-65	-63	-52	-48	-46	-62
3	Methyl		..	+45	+31	+23	+30	+31
4	Ethyl		..	..	+145	+102	..	..
4	Methyl		..	..	..	+62	+65	+19
5	Ethyl		..	..	..	..	+227	..
5	Propyl		..	..	..	..	..	+56
5	Methyl		..	..	..	..	..	+22
2 Methyl plus additional substitution as follows:								
2	Methyl		..	-102	-102	-75	..	..
3	Methyl		..	+20	+112	+95	+55	..
4	Ethyl		..	..	..	+154	..	..
4	Methyl		..	..	-94	-35	-18	-60
5	Methyl		..	..	..	-85	-35	..
6	Methyl		..	..	..	..	-51	-14
7	Methyl		..	..	..	..	..	-60
2,3	Methyls		..	..	+61	+145	..	..
2,4	Methyls		..	..	..	-110	..	..
2,5	Methyls		..	..	..	..	-99	..
2,6	Methyls		..	..	..	..	..	-89
3,3	Methyls		..	..	..	+230	+124	..
3,4	Methyls		..	..	..	+169	..	..
3,5	Methyls		..	..	..	..	-22	..
4,6	Methyls		..	..	..	..	..	-106
3 Methyl plus additional substitution as follows:								
3	Methyl		..	..	+93	+68	..	..
3	Ethyl		..	..	..	+246	..	..
4	Methyl		..	..	..	+167	..	..
6	Methyl		..	..	..	..	..	+60
3 Ethyl plus additional substitution as follows:								
3	Ethyl		..	..	..	..	342	..

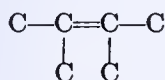
The effect of symmetry, or central grouping, is similar to the effect in the case of the paraffins. Thus,

$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\ | \quad | \\ \text{C} \quad \text{C} \end{array}$  has a density 0.0061 higher than that of heptene (1) but

$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\ | \quad | \\ \text{C} \quad \text{C} \end{array}$  has a density 0.0046 lower than heptene (1).

Both should be equally affected by the substitution of the hydrogen attached to the unsaturated carbon.

In the case of those olefins in which different factors produce a cumulative effect in the same direction, the change in physical properties is very large. Thus in the case of



with a compact central grouping and with substitution of hydrogen of both the unsaturated carbons, the density is 0.0349 higher than that of hexene (1) or 0.0268 higher than that of hexene (2).

### Averaged Data for Classes of Hydrocarbons

The large number of isomers for which data are now available makes it difficult to think in terms of the properties of individual hydrocarbons. In the case of much work on mixtures of hydrocarbons such as those obtained from petroleum by distillation (50, 67), averages for the different series for moderately wide boiling ranges (20° to 30° C.) are extremely valuable. Accordingly, the data in Table I to X have been averaged for seven boiling ranges between 10° and 200° C. in Table XIII.

In selecting the ranges, consideration has been given to convenience in the analysis of liquid hydrocarbon mixtures. The boiling ranges for which the data are averaged are as

follows: 10° to 40° C.; 40° to 70° C.; 70° to 100° C.; 100° to 125° C.; 125° to 150° C.; 150° to 175° C.; 175° to 200° C. These are approximately the same as those used by Kurtz and Headington (87) and by Thomas, Bloch, and Hoekstra (144). In special cases—for example, in mixtures containing a large amount of one compound the boiling point of which is almost identical with a cut point—it may be necessary to use other boiling ranges. For example, methylcyclohexane boils at 100° C. which is the dividing point between cuts 3 and 4; therefore, if much of this compound is present it would be desirable to take cut 3 from 70° to 90° C. and cut 4 from 90° to 120° C. However, the cuts given should prove satisfactory in most cases.

The number of compounds for which boiling point, density, and refractive index data are available is given immediately after the name of the type of compound; the boiling point at 760 mm. density ( $d_4^{20}$ ), refractive index ( $n_D^{20}$ ), and refractivity intercept ( $n - d/2$ ) are then listed in order. Following these are "derived dispersion" and "derived specific dispersion." These values were obtained by reading the specific dispersion corresponding to the average boiling point from the graph of specific dispersion vs. boiling point (see below), and then multiplying by the average density. This "derived dispersion," therefore, corresponds to the average density and average refractive index and may be used in connection with Equations 1 and 2 and the Sellmeier-Drude equation (88) to calculate the number and frequency of vibration of the dispersion electrons.

The use of the derived values was made necessary by the fact that the average data for the hydrocarbons for which dispersions have been reported are slightly different from corresponding data for all the known hydrocarbons boiling in the same range.

The latter part of each table presents the actual dispersion data which the authors have been able to tabulate. It is probable that there are more data on dispersion buried in the literature, and it is to be hoped that some one will attempt a more complete tabulation and correlation of dispersion data. Nevertheless it is not believed that future tabulations of dispersion data will make any radical change in the generalizations concerning dispersion given in this paper.

Many very interesting graphs showing the change in the density boiling point relation with change in structure can be prepared, as has previously been shown by the authors (156). It is intended in the present discussion to generalize in so far as possible the properties of each class of compounds; therefore, curves based on the table of averaged properties are presented (Figures 5 to 9, inclusive).

Such average curves, though useful, have the following limitations which should be kept in mind: (1) Because they represent the direct numerical average of all the tabulated data, compounds which are rare in nature are given equal weight with compounds known to be plentiful in nature; and (2) the deviation of particular compounds from the average curves may be large, especially in the case of the naphthenes. Since these curves do represent average data, they may be used more successfully in connection with data for relatively wide cuts (20° to 30° C.) than with narrow cuts (2° to 5° C.), as a more representative group of compounds will be found in a wide boiling range cut than in a very narrow cut. Density, refractive index, and refractivity intercept and dispersion are all additive on a volume per cent basis (156); there-



TABLE XIII. AVERAGE PROPERTIES FOR CUTS OF SPECIFIED BOILING RANGE

Class	Number of Compounds	Boiling Point	$d_4^{20}$	$n_D^{20}$	$n - d/2$	Derived Dispersion		Observed Dispersion			
						$F - C$	$\frac{F - C}{(F - C)/d} \times 10^4$	Number of compounds	Boiling point	$\frac{(F - C)}{\times 10^4}$	$\frac{(F - C)/d}{\times 10^4}$
Group 1, Boiling Range 10° to 40° C.											
Noncyclic											
Paraffins	2	32	0.6230	1.3556	1.0442	61.7	99	2	32	62.5	100
Monoolefins	6	32	0.6474	1.3771	1.0534	87.4	135	2	37	88.5	135
Nonconjugated diolefins	1	26	0.6594	1.3880	1.0583	101.5	154	..	...	...	...
Conjugated diolefins	1	34	0.6805	1.4216	1.0814	153.1	225	1	34	155	225
Monocyclic											
Naphthenes (all)	4	31.5	0.6791	1.3763	1.0368	67.2	99	1	33	72	106
Monoolefins	1	38	0.7105	1.4052	1.0500	83.8	118	1	38	...	...
Conjugated diolefins	1	40	0.8026	1.4429	1.0416	128.4	160	1	40	129	160
Group 2, Boiling Range 40° to 70° C.											
Noncyclic											
Paraffins	5	60	0.6575	1.3734	1.0446	65.1	99	5	60	65	99
Monoolefins	14	60	0.6783	1.3909	1.0517	88.2	130	5	65	89	129
Nonconjugated diolefins	4	62	0.6949	1.4095	1.0621	102.1	147	1	60	100	145
Conjugated diolefins	2	56.5	0.7038	1.4352	1.0832	155.5	221	2	56.5	156	221
Monocyclic											
Naphthenes (all)	2	51.5	0.7202	1.3967	1.0367	71.3	99	2	57.5	76	105
Monoolefins	1	44	0.7742	1.4230	1.0359	91.4	118	1	44	92	118
Conjugated diolefins	1	40	0.8026	1.4429	1.0416	128.4	160	1	40	129	160
Group 3, Boiling Range 70° to 100° C.											
Noncyclic											
Paraffins	10	89	0.6866	1.3884	1.0451	68.0	99	10	89	67	98
Monoolefins	27	87	0.7003	1.4012	1.0512	87.5	125	3	91	88	123
Nonconjugated diolefins	3	90	0.7206	1.4228	1.0625	102.3	142	1	92	105	145
Conjugated diolefins	9	80	0.7232	1.4465	1.0849	156.2	216	6	80	165	227
Monocyclic											
Naphthenes (all)	9	86	0.7509	1.4125	1.0371	74.3	99	5	89	75	98
Naphthenes (C <sub>6</sub> ring only)	2	90.5	0.7744	1.4253	1.0382	76.7	99	2	90.5	78.5	101
Monoolefins	3	86	0.7837	1.4334	1.0417	92.5	118	1	83	97	119
Conjugated diolefins	1	80	0.8405	1.4750	1.0548	148.8	177	1	80	149	177
Aromatics	1	80	0.8789	1.5012	1.0617	166.1	189	1	80	166	189
Group 4, Boiling Range 100° to 125° C.											
Noncyclic											
Paraffins	16	115	0.7096	1.3999	1.0451	70.3	99	10	116	70	100
Monoolefins	13	113	0.7249	1.4236	1.0530	89.2	123	5	121	88	122
Nonconjugated diolefins	3	114	0.7362	1.4327	1.0646	103.1	140	..	...	...	...
Conjugated diolefins	7	110	0.7451	1.4540	1.0814	156.5	210	3	109	160	215
Monocyclic											
Naphthenes (all)	16	117	0.7714	1.4252	1.0395	76.4	99	11	118	68.5	99
Naphthenes (C <sub>6</sub> ring only)	8	121.4	0.7785	1.4293	1.0401	77.1	99	6	122	76.8	99.7
Monoolefins	15	116	0.8010	1.4445	1.0441	94.5	118	5	...	93.5	117
Conjugated diolefins	2	111	0.8467	1.4835	1.0602	153.6	184	1	121	160	185
Aromatics	1	111	0.8670	1.4969	1.0633	159.5	184	1	111	160	185
Dicyclic											
Saturated	1	115	0.8043	1.4358	1.0337	79.6	99	..	...	...	...
Group 5, Boiling Range 125° to 150° C.											
Noncyclic											
Paraffins	12	139	0.7231	1.4071	1.0456	71.6	99	3	140	71	98
Monoolefins	7	142	0.7454	1.4247	1.0520	89.4	120	1	133	90	121
Nonconjugated diolefins	3	143	0.7654	1.4438	1.0611	105.6	138	2	144	106	138
Conjugated diolefins	8	142	0.7623	1.4604	1.0792	157	206	3	143	152	201
Monocyclic											
Naphthenes (all)	20	140	0.7863	1.4331	1.0401	77.8	99	16	139	77	99
Naphthenes (C <sub>6</sub> ring only)	12	140	0.7895	1.4356	1.0408	78.2	99	9	139	70	99.5
Monoolefins	23	138	0.8125	1.4513	1.0451	95.9	118	11	139	97	119
Conjugated diolefins	4	135	0.8359	1.4815	1.0637	158	189	1	136	162	192
Aromatics	4	139	0.8677	1.4981	1.0643	154.4	178	4	139	157	181
Dicyclic											
Saturated	6	142	0.8382	1.4514	1.0323	83	99	1	132	79	99
Tricyclic											
Saturated	1	145	0.8600	1.4522	1.0222	85	99	1	145	87	101
Group 6, Boiling Range 150° to 175° C.											
Noncyclic											
Paraffins	16	163	0.7348	1.4135	1.0461	72.7	99	6	165	72	99
Monoolefins	7	162	0.7499	1.4286	1.0537	89.2	119	3	161	89	119
Nonconjugated diolefins	6	162	0.7772	1.4475	1.0590	107.2	138	2	165	106	138
Conjugated diolefins	4	165	0.7792	1.4629	1.0734	158.2	203	..	...	...	...
Monocyclic											
Naphthenes (all)	18	162	0.7974	1.4385	1.0399	78.9	99	9	164	79	99
Naphthenes (C <sub>6</sub> ring only)	13	164.1	0.8027	1.4413	1.0400	79.5	99	8	165	79.1	99
Monoolefins	14	160	0.8175	1.4557	1.0470	96.5	118	4	159	96	118
Conjugated diolefins	2	169	0.8365	1.4804	1.0622	162	194	2	169	150	169
Aromatics	11	166	0.8679	1.4963	1.0624	149.3	172	10	165	148	170
Dicyclic											
Saturated	7	161	0.8544	1.4593	1.0321	84.6	99	1	163	82	93
Group 7, Boiling Range 175° to 200° C.											
Noncyclic											
Paraffins	4	190	0.7515	1.4229	1.0472	74.4	99	1	195	74	100
Monoolefins	3	186	0.7661	1.4362	1.0532	90.4	118	..	...	...	...
Monocyclic											
Naphthenes (all)	11	187	0.8037	1.4430	1.0412	79.6	99	1	178	77	97
Naphthenes (C <sub>6</sub> ring only)	11	187.9	0.8037	1.4430	1.0412	79.6	99	1	178	77	97
Monoolefins	9	187	0.8212	1.4578	1.0472	96.9	118	1	182	94	116
Aromatics	26	189	0.8680	1.4965	1.0625	145.8	168	10	185	145	167
Dicyclic											
Saturated	5	184	0.8677	1.4673	1.0333	85.9	99	..	...	...	...
Tricyclic											
Saturated	1	184	0.885	1.4688	1.0261	87.6	99	..	...	...	...



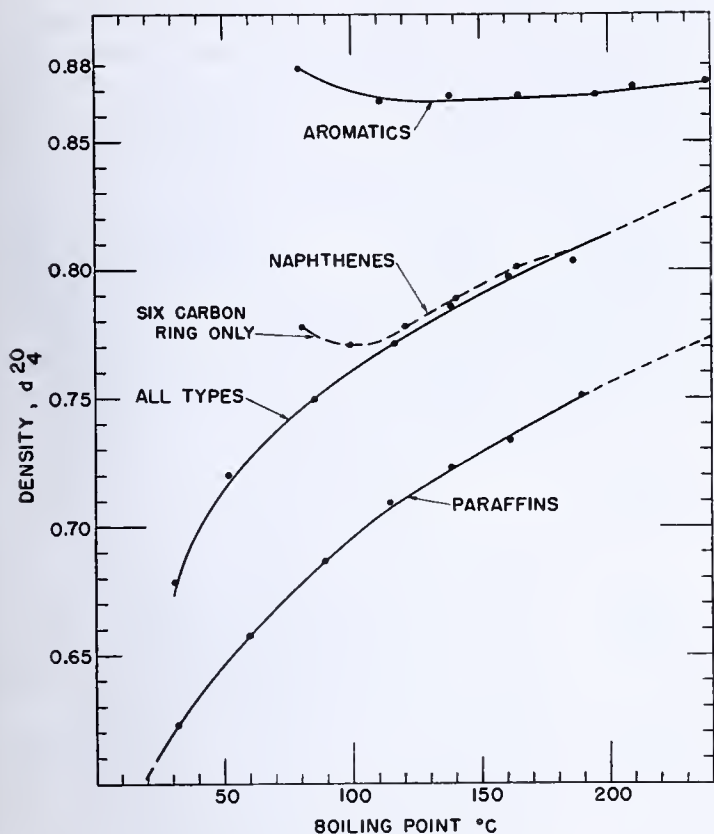


FIGURE 5. DENSITY-BOILING POINT RELATIONSHIP FOR PARAFFINS, NAPHTHENES, AND AROMATICS

fore a direct numerical average of these properties is equivalent to the value which should be obtained on mixing equal volumes of all the compounds averaged. Specific dispersion, on the other hand, is additive on a weight per cent and boiling point approximately on a mole per cent basis. For the relatively narrow cuts concerned in Table XIII the difference between volume per cent, weight per cent, and mole per cent, will be small, but in the case of the general average over the range 10° to 200° C. the distinction must be kept in mind. Fortunately, all the properties needed for solving the Sellmeier-Drude equation are additive on the same basis—namely, the volume per cent basis.

In Figure 5 the densities of the three hydrocarbon series occurring naturally in petroleum are plotted against boiling point. The naphthenes (defined as saturated monocyclic compounds) containing six carbon atoms in the ring are plotted separately in order to bring out the relation between the six-ring saturated cyclics and the aromatics.

Figure 6 for cyclic and noncyclic olefins is drawn on the same scale as Figure 5. It is clear that the noncyclic olefins fall between the paraffins and naphthenes in density and that the cyclic olefins fall between the naphthenes and the aromatics.

Figure 7 for the refractivity intercept *vs.* boiling point shows the small but significant change in refractivity intercept with increase in boiling point. As pointed out in the original discussion (88) of this relationship, the intercept could have been made more constant for the homologous series by using a slope slightly greater than 0.5 in the intercept equation, but since in groups of hydrocarbon isomers the slope is approximately 0.485, a mean slope of 0.5 was chosen. The relatively uniform spacing of the curves for the noncyclic monoolefins, the paraffins, and the one-, two-, and three-ring cyclics suggests a roughly uniform increment for the addition or removal of two hydrogens when conjugation is not involved.

Taking the general average for the range 10° to 200° C. the increments are as follows:

	Increment of Intercept
Monoolefins to paraffins	67
Paraffins to monocyclic saturated	60
Monocyclic to dicyclic saturated	69
Dicyclic to tricyclic saturated	84

As data for only two tricyclic saturated compounds boiling in this range are available, the last increment is admittedly uncertain.

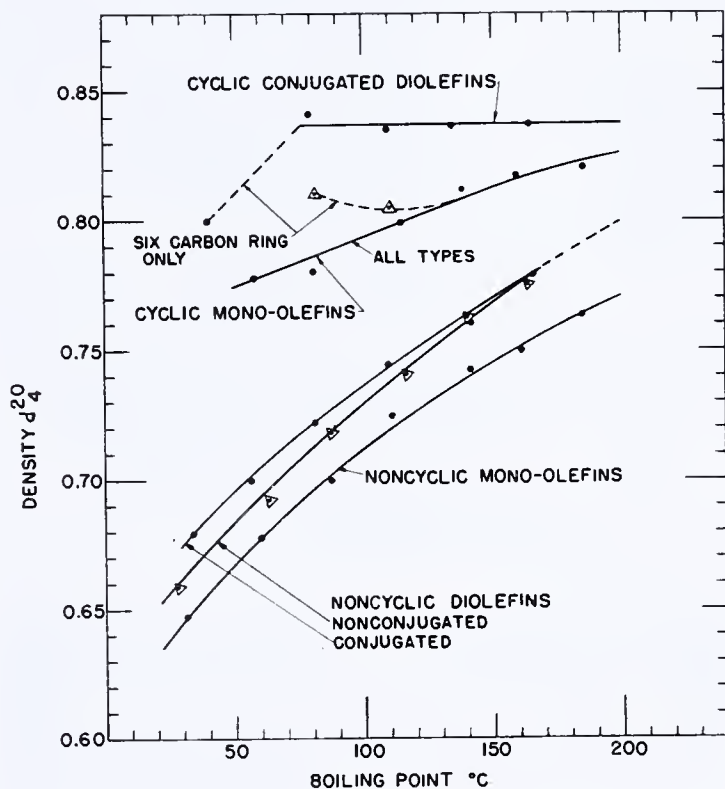


FIGURE 6. RELATION OF DENSITY TO BOILING POINT FOR UNSATURATED COMPOUNDS

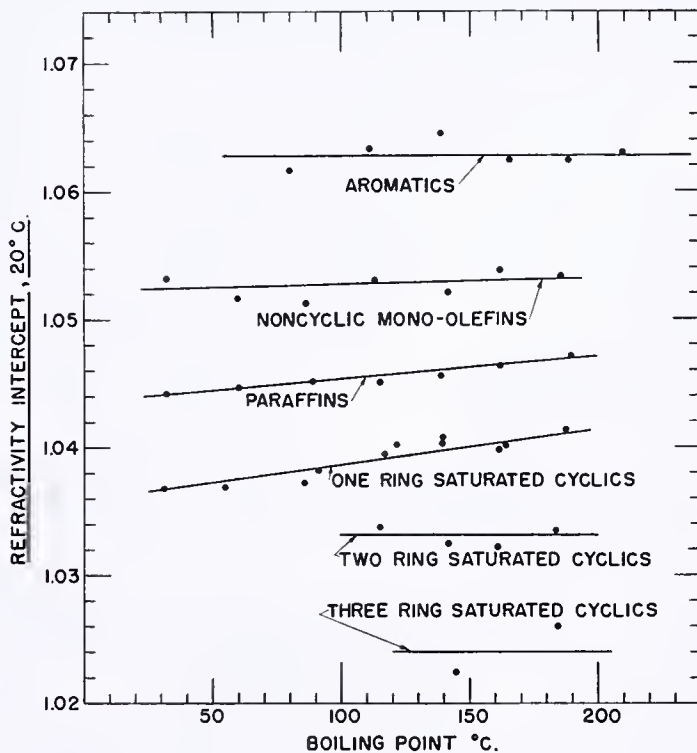


FIGURE 7. REFRACTIVITY INTERCEPT *vs.* BOILING POINT FOR PARAFFINS, NAPHTHENES, AROMATICS, AND NONCYCLIC MONOOLEFINS



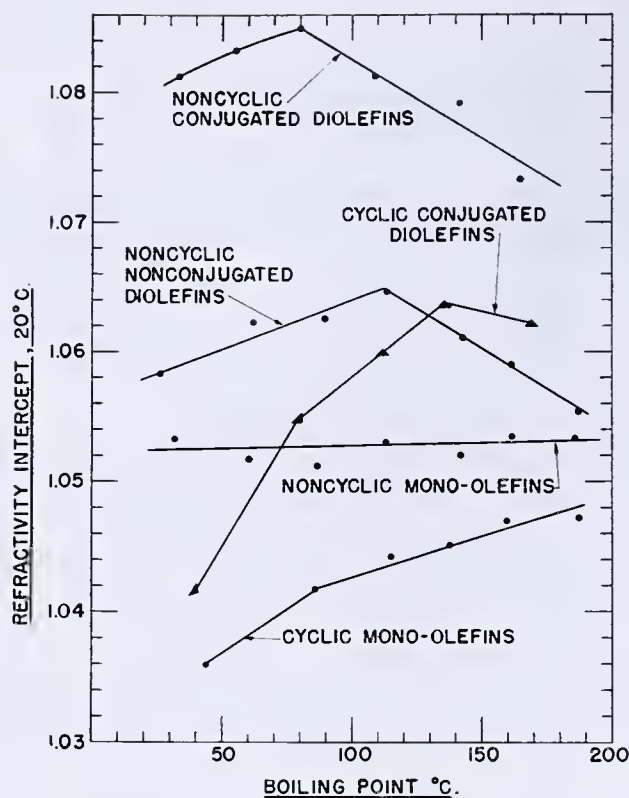


FIGURE 8. REFRACTIVITY INTERCEPT *vs.* BOILING POINT FOR CYCLIC AND NONCYCLIC OLEFINS AND DIOLEFINS

Figure 8 for the intercepts of various classes of olefins shows peculiar peaks in the range 80° to 140° C. for the diolefins whether conjugated or nonconjugated. The reason for these peaks has not yet been determined. Since there is much scattering of data within each group, the peculiar trend of the average curves for the diolefins may possibly be the result of poor data. The authors are, however, inclined to believe that there is some fundamental reason for these peaks and hope to find out just what it is.

Figure 9 for the specific dispersion  $(n_F - n_C)/d$  of various classes of hydrocarbon is extremely interesting because it presents many striking regularities. These may be summarized as follows:

All saturated compounds have specific dispersions of approximately 0.0099, irrespective of boiling point.

Cyclic monoolefins have specific dispersions of approximately 0.0118, irrespective of boiling point.

Noncyclic monoolefins of low boiling point have specific dispersions as high as 0.0135, but as their boiling point increases the specific dispersion decreases to the same value as the cyclic monoolefins.

The specific dispersions curve for unconjugated noncyclic diolefins is above the curve for the corresponding monoolefins, but is substantially parallel to it.

The specific dispersions curves for the cyclic and noncyclic conjugated diolefins converge towards one another as boiling point increases.

Substitution in the benzene ring decreases the specific dispersion.

With the aid of curves of this type it is possible to estimate with considerable accuracy the specific dispersions of hydrocarbons belonging to the classes shown, provided the boiling point is known. If the density is known the dispersion can be calculated, and with the aid of Equations 1 and 2 and  $n_D^{20}$  it is possible to calculate the refractive index for the *C* and *F* lines.

This makes it possible to solve the Sellmeier-Drude equation for many compounds for which experimental dispersion data are not available.

Finally, for ready reference, the data for 459 hydrocarbons boiling from 10° to 200° C. have been averaged in Table XIV. This table should be used in connection with Figures 5 to 9 because the fact that the average boiling points of the known compounds of the different series are different introduces some apparent distortions. Thus the density of the average noncyclic olefin is slightly lower than that of the average paraffin because the average boiling point is 20° lower. However, Table XIV gives an excellent condensed picture of the physical

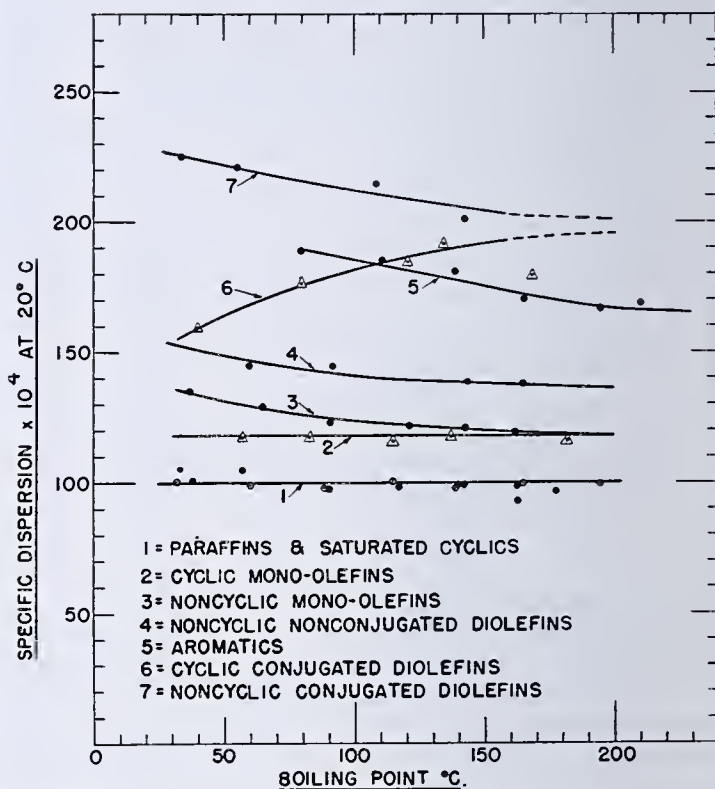


FIGURE 9. RELATION OF SPECIFIC DISPERSION TO BOILING POINT FOR EIGHT SERIES OF HYDROCARBONS

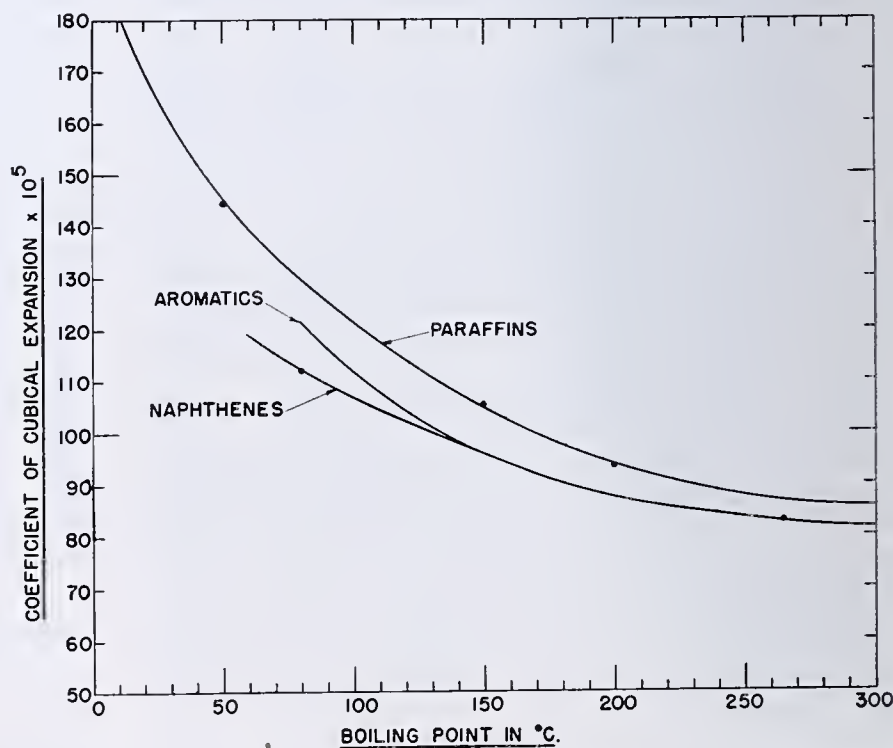


FIGURE 10. COEFFICIENT OF CUBICAL EXPANSION *vs.* BOILING POINT FOR AROMATICS, NAPHTHENES, AND PARAFFINS



TABLE XIV. AVERAGE PROPERTIES OF KNOWN COMPOUNDS IN CUTS OF SPECIFIED BOILING RANGE

Class	(Groups 1 to 7. Boiling range, 10° to 200° C.)		$d_4^{20}$	$n_D^{20}$	$n - d/2$	Derived $\times 10^4$ $F - C$	Dispersion $(F - C)/d$
	No. of Compounds	Boiling Point °C.					
Noncyclic Paraffins	65	121.7	0.7085	1.3998	1.0455	70.4	99.0
Monolefins	77	101.8	0.7075	1.4058	1.0521	88.3	124
Nonconjugated diolefins	20	112.1	0.7384	1.4304	1.0612	104.3	143
Conjugated diolefins	31	111.7	0.7430	1.4524	1.0809	156.6	211
Monocyclic Naphthenes (all)	80	133.1	0.7772	1.4281	1.0395	76.9	99
Naphthenes (C <sub>6</sub> ring only)	46	152.0	0.7942	1.4376	1.0405	78.6	99
Monolefins	66	135.3	0.8087	1.4496	1.0453	95.5	118
Conjugated diolefins	10	121.0	0.8353	1.4772	1.0596	154	185
Aromatics	43	176.6	0.8682	1.4968	1.0627	148	171
Dicyclic Saturated	19	159	0.8501	1.4576	1.0326	84.1	99.0
Tricyclic Saturated	2	164.5	0.8725	1.4604	1.0242	86.3	99

properties of the different hydrocarbon series in comparison to each other. This is particularly true of the refractivity intercepts, dispersions, and specific dispersions.

### Effect of Temperature and Pressure on Density and Refractive Index

Various methods of generalizing the change of density for °C. for different types of compounds were tried. The method of Beale (19), in which cubical coefficient of expansion is plotted against boiling point, has the merit that the curves for the paraffins and the aromatics are approximately parallel. This lends strength to the idea that this method of plotting is fundamentally sound.

Figure 10 for the cubical coefficient of expansion *vs.* boiling point is almost identical with that of Beale (19) as far as paraffins and aromatics are concerned. Data for 22 naphthenes were plotted on this type of graph. The data for the higher boiling naphthenes were erratic and scattered on both sides of the curve for the aromatics. It was therefore decided not to attempt at this time to draw separate curves for the higher boiling aromatics and naphthenes. Data for 32 cyclic unsaturated compounds showed similar scattering around the aromatic-naphthene curve; therefore, it is recommended that the naphthene curve be used for these compounds also. Similarly, in the case of the noncyclic olefins and diolefins, there is at present an insufficient amount of reliable data to justify a curve distinct from that for the paraffins. Accordingly, the paraffin curve is recommended for all noncyclic hydrocarbons.

The cubical coefficient of expansion is useful, since when multiplied by the density it yields the increment of density change per degree change in temperature.

Figure 11 is derived by multiplying the cubical coefficient of expansion obtained from Figure 10 by the densities read from Figures 5 and 6. In addition, the density change data from the unabridged petroleum tables (107) have been plotted. It is significant that as density increases in each homologous series, other than the aromatics, the curve for each series tends to bend towards the curve for petroleum. The accentuated divergence between the curves for the saturated cyclic with six-membered rings and all saturated cyclic is also of interest.

Figure 12 has been prepared as an aid in correcting from specific gravity at 60° F., which is the usual standard in the petroleum industry, to  $d_4^{20}$  which is needed for calculating the refractivity intercept or specific dispersion at 20° C. This curve involves the coefficient of expansion based on the unabridged National Standard Petroleum Tables and the change in density of water between 60° F. (15.56° C.) and 40° C.

Figures 11 and 12 are, of course, intended primarily as a practical aid in correcting densities to 20° C. when they are found in the literature at other temperatures. The corresponding refractive index correction will be given with reasonable accuracy by the equation

$$\Delta n = 0.60 \Delta d \quad (3)$$

This equation is based both on the Eykman equation and on empirical observation (88, 156). In case refractive index data are to be corrected over a wide range for the effect of either pressure or temperature, the Eykman equation can be used with confidence provided the change in density is known (57, 88, pp. 697-704). It is also possible, as shown by Kurtz and Ward (88, p. 723) to express the relationship between refractive index and density by means of an equation of the Sellmeier-Drude type in which a coefficient for the effect of tem-

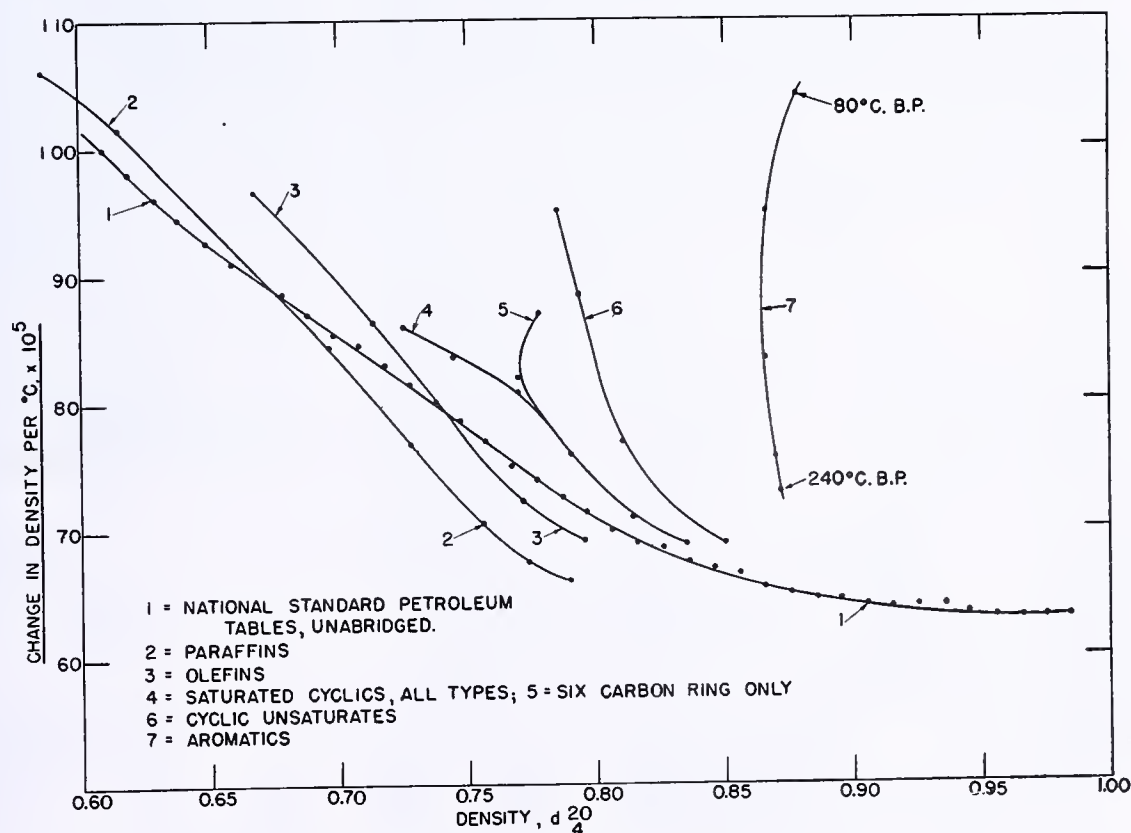


FIGURE 11. CHANGE IN DENSITY PER DEGREE CHANGE IN TEMPERATURE *vs.* DENSITY FOR FIVE HYDROCARBON SERIES AND FOR PETROLEUM



perature or pressure on the frequency of vibration of the dispersion electrons is introduced. The coefficient of frequency change is fortunately proportional to the density change; therefore, if the change in density with temperature or pressure is known, the change in refractive index can be calculated. For example, the excellent data of Gibson and Kincaid (57) for the effect of pressure and temperature on benzene are, as shown by Table XV, accurately represented by the equation

$$n^2 - 1 = \frac{B}{(V_0 + \phi)^2 - V^2}$$

(4)

where  $n$  = the refractive index  
 $B$  = a constant characteristic of each compound =  
dispersion electrons per gram  $\times$  density =  
 $\frac{1.2403 \times 10^{-8}}{6.0886 \times 10^{30} \times \text{density}}$   
 $V_0$  = characteristic frequency of dispersion electrons in  
benzene =  $2.1288 \times 10^{15}$   
 $V$  = frequency of light used;  $V^2 = 0.47344 \times 10^{30}$  for  
hydrogen line at 436  $m\mu$ ;  $V^2 = 0.25892 \times 10^{30}$  for  
average sodium line at 589  $m\mu$   
 $\phi$  = increment of frequency of dispersion electrons due  
to effect of temperature or pressure =  $(0.87366 -$   
density)  $3.14 \times 10^{14}$

This equation was obtained by interpolation, using the Eykman equation to obtain refractive indices for the 589 and 436 lines at the same pressure, then solving for  $B$  and  $V_0$ . The number of electrons per gram was found to be reasonably constant, the average value being  $7.5517 \times 10^{22}$ . As previously shown,  $B = \frac{\text{density} \times \text{electrons per gram}}{1.2403 \times 10^{-8}}$ . Therefore in this case,  $B = \text{density} \times 6.0886 \times 10^{30}$ . From the point of view of ease of use, the Eykman equation is in some respects more simple than Equation 4. From a theoretical point of view, it is very significant that the effect of temperature or pressure on the relationship between density and refractive index can be accurately represented by an equation in the Sellmeier-Drude form, provided the frequency of vibration is corrected for the

TABLE XV. CALCULATION OF REFRACTIVE INDEX OF BENZENE FROM DENSITY AT VARIOUS TEMPERATURES AND PRESSURES (Using the modified Sellmeier-Drude equation containing a coefficient for the change in frequency at vibration of the dispersion electrons, using data of Gibson and Kincaid)

Wave Length $m\mu$	Tem- pera- ture $^{\circ}$ C.	Pressure in Bars	Density	Calcd. $n$	Obsd. $n$	$\Delta n \times 10^4$
589	25	1	0.87366	1.4983	1.4983	0
		272	0.89430	1.5108	1.5108	0
		617	0.91580	1.5239	1.5240	-1
		868	0.92927	1.5322	1.5323	-1
	45	1	0.85220	1.4853	1.4851	+2
		547	0.89460	1.5110	1.5108	+2
		919	0.91618	1.5242	1.5242	0
		1188	0.92959	1.5324	1.5324	0
436	25	1	0.87366	1.5201	1.5201	0
		26	0.87576	1.5214	1.5212	+2
		343	0.89911	1.5363	1.5365	-2
		561	0.91264	1.5450	1.5449	+1
	45	1	0.8522	1.5065	1.5065	0
		280	0.8760	1.5215	1.5214	+1
		629	0.8997	1.5367	1.5366	+1
		867	0.9134	1.5455	1.5450	+5

influence of temperature or pressure in accordance with Equation 4 of this paper or Equation 66 of a previous paper (88). It will be observed that in 16 calculations, the difference between the calculated and observed refractive index was greater than 0.0002 in only one instance.

Acknowledgment

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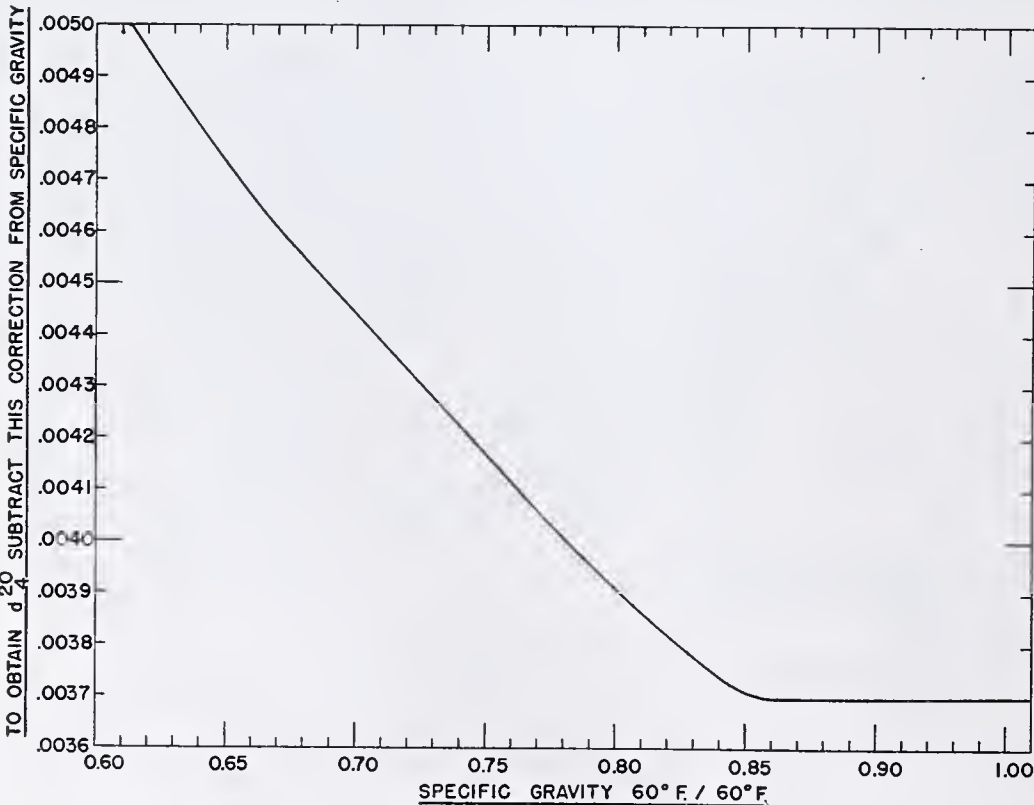


FIGURE 12. CONVERSION FROM SPECIFIC GRAVITY 60/60° F. TO DENSITY 20/4 FOR PETROLEUM



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# Determination of Mercury with s-Diphenylcarbazine

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THE reaction of mercuric ions with s-diphenylcarbazine to yield a purple aqueous solution is recognized as a very sensitive reaction, given by one part of mercury in 100,000 parts of water (1, 5). The methods of obtaining the mercury from the sample and the preparation of the aqueous solution have been carefully studied (6, 8, 9). This reaction is influenced by many factors, such as the pH of the solution, exposure to air, ratio of reagent to metal, etc., but no systematic investigation of these influences has been reported in the literature. The purpose of the present paper is to describe a study of the conditions necessary for the accurate determination of mercury with diphenylcarbazine.

## Apparatus and Methods

The color determinations were made with a photoelectric colorimeter (a description of which is soon to be published), designed by C. W. Fleetwood of this laboratory. It uses as its light-measuring elements two Weston photonic cells, which are electrically opposed, and the current developed by them is balanced by means of a variable resistance. When a colored solution is interposed between one cell and the source of light, this variable resistance,  $R_3$ , is adjusted until balance is again restored. The light absorption of the solution is thus measured in terms of the ohms required to secure the balance. A sensitive galvanometer serves as the indicating instrument. All measurements were made in 10-cm. cells.

All pH measurements were made with a glass electrode, in the circuit of which was inserted a vacuum-tube apparatus operating at the open grid potential.

Standard solutions of mercury were prepared by dissolving weighed amounts of Mallinckrodt's analytical reagent quality mercuric chloride, mercuric nitrate, and mercuric sulfate, respectively, in triple-distilled water. The s-diphenylcarbazine was obtained from the Eastman Kodak Company and showed a melting point of 172–173°. All weights, pipets, burets, and volumetric flasks were calibrated by standard methods.

## The Reagent

Absolute alcohol was found to be the most satisfactory solvent for the diphenylcarbazine and a 1 per cent (approximately saturated) solution the most desirable concentration. The minimum amount of alcohol was necessary because the rate of color destruction of the mercury solutions is proportional to the alcoholic content. Since the reagent solution was found to discolor upon standing for 24 hours, it was always prepared during the day on which it was used. It was preserved in a glass-stoppered bottle and stored in a dark place, since light and atmospheric oxygen hastened the discoloration.

## The Color Reaction

The curve in Figure 1 shows the extent to which the color is dependent on the mercury concentration over the range studied. The intensity of the color developed upon the addition of the diphenylcarbazine was found to be independent of the amount of the latter, provided the ratio of the reagent to the mercury was 2 to 1 or greater. This ratio might serve as evidence that the colored product is Feigl and Lederer's (2) inner metal complex (a carbazine) with the formula  $\text{Hg}_2\text{Dc}$  and not a carbazone as suggested by Cazeneuve (1), Stock and Zimmermann (8), and others.

## Rate of Color Formation

In all the work with the mercury solutions, the maximum color intensity was attained within 15 minutes after the addition of the diphenylcarbazine. The order of mixing the reagent and mercury solution, the amount of stirring, and the concentration of the metal had no effect on the rate of color formation. However, the procedure followed was to pipet the reagent drop by drop into the Erlenmeyer flask containing



the mercury solution, shaking the flask after the addition of each drop. No fading of the color solution occurred within a period of several hours, provided the solutions were not unduly exposed to atmospheric oxygen.

### Influence of Various Ions

Stock and Pohland (7) report that the mercury determination cannot be made in the presence of zinc, iron, cobalt, nickel, lead, copper, silver, gold, cyanides, bromides, or iodides (these latter three can be present in minute quantities). These same authors find that sodium, potassium, ammonium, magnesium, calcium, strontium, barium, aluminum, manganese, fluorides, and chlorides (provided the concentration of the latter two is not large) are without influence upon the determination. Obviously, chromate ions must be absent, since even in strongly acid solutions they give an intense violet color with diphenylcarbazide (1).

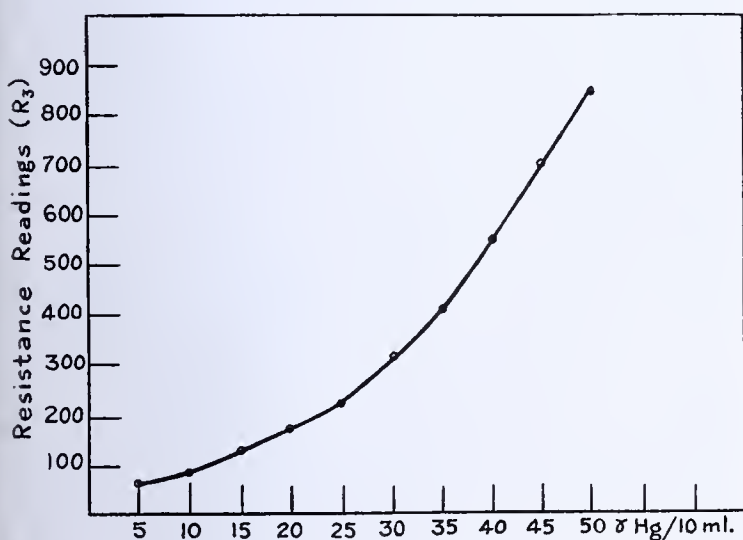


FIGURE 1. RELATION OF COLOR INTENSITY TO MERCURY CONCENTRATION

Preliminary work verified the above findings with some exceptions. Zinc did not interfere until the concentration was five times that of the mercury. Cadmium was found to belong to the noninterference list and chlorides were found to have a very destructive action upon the colored mercury compound. In view of the fact that free chlorine is frequently used in getting mercury into solution (6, 8, 9), a quantitative study of the influence of chloride ions was made.

The results showed that the chloride ion, whether the anion of a metal or the acid, caused, not a flocculation of the colored compound but a decomposition into colorless soluble products. A chloride-ion concentration greater than 0.0001 *N* (3.5 mg. per liter) produced the color destruction.

Majer's (4) conclusion that ammonium ions also have a destructive effect on the colored mercury compound was verified. However, he attributed a much greater effect to the ammonium ion than the authors' experiments would justify. This lack of agreement is probably due to the fact that Majer studied the effect of ammonium chloride instead of an ammonium salt in which the anion had no influence. The presence of ammonium ions up to a concentration sufficient to cause precipitation gave readings only slightly lower than solutions of like mercury contents without ammonium ions, and the destructive effect produced by ammonium chloride was only slightly greater than that caused by an equivalent amount of sodium chloride.

All work with the influence of the various ions indicated

that the greater the electrolyte concentration the greater the precipitation tendency of the colored mercury compound. The nitrates and sulfates of potassium, sodium, and ammonium were chosen as typical salts and the influence of various concentrations on the precipitation time was noted. The presence of these salts was found to be without influence until the concentration reached 0.003 *N* to 0.004 *N* (200 to 400 mg. per liter depending upon the molecular weight) when precipitation took place in less than an hour. Precipitation usually occurred sooner in solutions containing ammonium salts than in those containing an equivalent amount of the corresponding sodium or potassium salt.

Flocculation studies made with solutions of pH values ranging from 3.5 to 6.3 showed that the higher the pH the greater the tendency to precipitation. In fact, at a pH above 6, a precipitate frequently appeared in a short time without the presence of an electrolyte. Another feature noted was that the higher the concentration of mercury, the smaller the concentration of electrolyte needed to cause flocculation of the colored mercury compound.

### Hydrogen-Ion Concentration

Above a pH of 7 the diphenylcarbazide functions as a hydrogen-ion indicator, the colorless solution taking on an orange hue. The hydrogen-ion concentration also has a decided influence on the reaction between mercuric ions and diphenylcarbazide. Stock and Zimmermann (8) reported that the reaction is best carried out in a neutral solution and suggested the use of either urea or sodium acetate (the choice depending upon the concentration of mercury) to adjust the pH. Thilenius and Winzer (9) gave a pH of 3 to 4 as the maximum stability value, but apparently did not differentiate between the influence of the hydrogen ion and that of the chloride ion. In this work a more extensive study of the effect of the hydrogen-ion concentration was made and the optimum pH range for the color reaction was determined. The experiments showed that the color could exist with varying intensities over a fairly wide pH range (approximately 2.6 to 7); below 2.6 the solution was decolorized and above 7 the color effect of the reagent interfered. It was evident, therefore, that if solutions are to be compared accurately, the pH values must either be similar or in a range where there is little variation of color intensity with pH. Attempts to buffer the mercury solutions with urea were unsuccessful; the addition of urea did not satisfactorily adjust the pH and greatly increased the flocculation tendency of the mercury diphenylcarbazide.

Attempts to buffer the solution by the addition of a saturated sodium acetate solution failed because the pH values of the treated solutions frequently differed so much that solutions of like mercury concentrations gave unlike readings.

A study was made to find the pH range in which the color intensity of mercury solutions of the same concentration showed the smallest variation. This was found to be from 3.5 to 4.5. Therefore, a pH value of 4 was considered the optimum for mercury determinations with diphenylcarbazide. However, although the shift in color is less pronounced between pH 3.5 and 4.5, even between these limits it is great enough to require holding the pH constant within  $\pm 0.3$  unit for accurate determinations.

It was found that a satisfactory adjustment of pH values could be accomplished with a precision of  $\pm 0.1$  pH unit by titrating with dilute acetic acid or sodium acetate, using the glass electrode as an indicator. The precision with bromophenol blue as the indicator was slightly less, but still sufficient for accurate determinations. These titrations with a colored indicator were performed on an aliquot portion, not on the solution to which the diphenylcarbazide was added.



The addition of either acetic acid or sodium acetate did not interfere with the color reaction, provided that the total electrolyte concentration did not exceed the salting out value and cause the precipitation of the colored complex.

The use of potassium acid phthalate as a buffer was abandoned, since precise results were not obtained with it.

### Lambert-Beer Law

According to the Lambert-Beer law and the electrical setup of the colorimeter, the molecular concentration of mercury,  $c$ , should be a linear function of  $\log(1 + \frac{R_3}{R_2})$ , where  $R_2$  represents the fixed resistance and  $R_3$  the number of ohms necessary to restore balance when the colored solution is placed between the source of light and photonic cell. As is shown in Figure 2, the colored mercury solutions did not con-

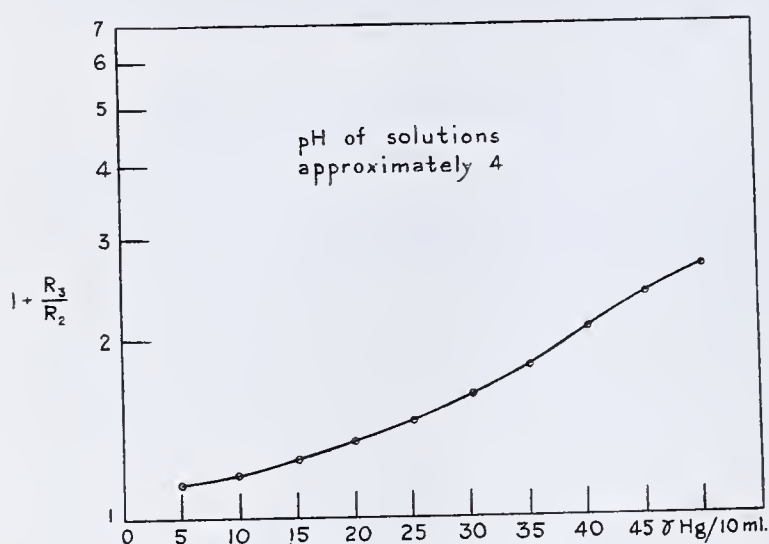


FIGURE 2. CONFORMITY OF COLORED SOLUTIONS TO THE LAMBERT-BEER LAW

form to this linear relationship predicted by the Lambert-Beer law over the total range of concentrations studied (5 to 50  $\gamma$  of mercury per 10 ml.). However, an examination of Figure 2 shows that the law is followed within the experimental error over somewhat smaller ranges of concentration.

### Sensitivity

The sensitivity data for mercury solutions of pH values of approximately 4 are given in Table I.

The number of milligrams of mercury producing a perceptible difference in 20 ml. of solution is designated by  $\Delta$  and listed in the third column. In the first column are listed the volumes in liters containing one gram atom of mercury. Column  $B$  represents the total number of milligrams of mercury in 20 ml. of solution. The sensitivity,  $S$ , is the reciprocal of the figure recorded in column 3.  $B' = B + \Delta$ .

The values of  $S$  indicate that the sensitivity is approximately the same at the different concentrations until a concentration of 0.09 mg. per 20 ml. is reached, when the sensitivity decreases. There is also a smaller decrease in sensitivity at a concentration of 0.03 mg. per 20 ml.

Horn (3) has suggested that the ratio  $B/B'$  is probably constant throughout colorimetry, independent of the color examined. He found this true in the case of  $\text{CrO}_4^{--}$ ,  $\text{Cu}^{++}$ , and  $\text{Cu}(\text{NH}_3)_4^{++}$ , respectively. Yoe and Hill (11), Yoe and Wirsing (12), and Yoe and Hall (10) have extended this investigation to other colored solutions and have likewise found that the  $B/B'$  ratio is approximately a constant, with a value

around 0.90 to 0.95. The values obtained in this work for mercury are slightly higher than previously determined  $B/B'$  ratios, although one is hardly justified in making this comparison since the values of previous experimenters were obtained by visual observations.

TABLE I. SENSITIVITIES AT VARIOUS MERCURY CONCENTRATIONS

$V$	$B$	$\Delta$	$S$	$B'$	$B/B'$
401,220	0.01	0.00074	1,350	0.01074	0.930
133,726	0.03	0.00085	1,176	0.03085	0.972
80,244	0.05	0.00074	1,350	0.05074	0.985
57,173	0.07	0.00072	1,398	0.07072	0.989
44,576	0.09	0.00096	1,041	0.09096	0.989

### Summary

The colorimetric method of determining mercury with diphenylcarbazide necessitates a careful control of experimental conditions if accurate results are to be obtained.

The reagent should be dissolved in absolute alcohol and a fresh solution should be prepared each day. The intensity of the color developed by the mercury solution is independent of the reagent concentration, if its ratio to the mercury is 2 to 1 or greater.

The maximum color intensity is attained within 15 minutes after the addition of the reagent.

The solutions must be free from chloride ions. The presence of ammonium ions gives slightly low results. An electrolyte concentration greater than 0.003  $N$  usually causes the colored mercury compound to precipitate in less than an hour.

The color is greatly influenced by the pH of the solution. A pH of 3.5 to 4.5 is suitable, but for a given series of comparisons the value must be held constant to 0.3 pH unit if the error from this source is not to exceed 5 per cent. A satisfactory pH may be secured by titration on an aliquot of the sample solution with dilute acetic acid or sodium acetate, using either the glass electrode or bromophenol blue as the indicator.

If the foregoing experimental conditions are observed, and the thickness of the solution layer is 10 cm., diphenylcarbazide will determine quantitatively as little as 0.4 mg. of mercury in a liter of solution with a precision of approximately 5 per cent. For quantities ranging from 5 to 50  $\gamma$  per 10 ml. the average precision is about 3 per cent. When a colorimeter of the Duboscq type with setting at 20 was used for the observations, the sensitivity was decreased. Precise determinations could not be made on solutions containing less than 0.8 mg. of mercury per liter. No attempt was made to increase the sensitivity in either method by using color filters.

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# Quantitative Spectrographic Estimation of Trace Elements in Biological Ash

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**P**ROBLEMS dealing with mineral content of foods are of interest not only because of their biological bearing but also because of the general type of analytical methods which must be employed. Very accurate gravimetric and volumetric analyses have been developed for the elements present in large quantities, such as sulfur, phosphorus, sodium, potassium, magnesium, and calcium. However, for most other elements these methods require a larger amount of material than is available from samples of reasonable size. Where only small samples are available, spectrographic methods have been used for the analysis of the elements present in relatively high concentrations (2, 3), but no attempts have been made to estimate quantitatively the amounts of such trace elements as vanadium, copper, silver, aluminum, and titanium, which might be present in concentrations of only a few parts per million. Interest was aroused in this work in connection with a problem in poultry nutrition.

This work was carried out in an attempt to correlate the quality of hen's eggs with the mineral content of the whites and yolks. The relative analyses of highly viscous and relatively nonviscous eggs are known for sodium, potassium, magnesium, phosphorus, and calcium, but only qualitative analyses have been made for the "trace" elements (1). Various methods of quantitative spectrographic analysis have been reported in the literature: the method of homologous lines (4, 7, 8), the customary method of exposing spectra of the samples and of the corresponding standards alternately on the same film (6), and an internal standard element used in connection with light-intensity measurements (2).

In order to facilitate the analysis of a large number of samples the method of standard curves was employed (3). While this method does not give the ultimate in precision, it lends itself to the quantitative estimation of metallic content of many types of samples where several elements are present, and gives reproducible results.

## Apparatus and Technic

A Central Scientific Company replica, 20,000 lines per 2.5-cm. (1-inch) grating with a focal length of 106 cm., was used in this investigation. The dispersion of the instrument was 8.7 Å. per mm. at 2500 Å. and 10.0 Å. per mm. at 4000 Å. The method of excitation of the sample was that described previously (3, 6). Graphite rods of the best spectrographic grade obtainable from Bausch & Lomb Optical Company were used. They were 7.8 mm. (0.3 inch) in diameter and about 5 cm. (2 inches) in length. The lower electrode, which served as anode, contained a well for the sample 9.4 mm. (0.375 inch) in depth and 4.7 mm. (0.19 inch) in diameter. Both electrodes were mounted vertically.

Two hundred and twenty volts direct current were used with a heavy ballast resistance. The current was maintained at 9 amperes during exposures by adjustment of the gap distance. The graphite electrodes were refluxed in concentrated nitric acid vapors for 4 days to eliminate traces of iron and vanadium which were found to be present after drilling the well, and were then refluxed in triple-distilled water and dried at 110° C. Since only very small amounts of the ash were available for analysis, the samples were treated in the following manner:

The concentration used was 0.00676 gram per cc. This particular value was used only because the amount of the smallest sample was such as to make this concentration convenient in the glassware available. The dry ash was weighed directly in small calibrated flasks, pure concentrated nitric acid was added, and the solutions were digested for 8 hours at 100° C. and finally made up to volume. No base material was added, as has been recommended (3), since it was shown that the large quantities of sodium, potassium, magnesium, calcium, and phosphorus present

were sufficient to cause the arc to run smoothly. The previously treated graphite electrodes were arced for 1 minute to drive off any traces of impurities and to increase the porosity. After cooling, 0.6 cc. of the sample solution was added by repeated additions and drying. This method of successive additions was necessary in order to put enough sample in the anode electrode. Using this amount of solution, 4.06 grams of ash were deposited in the anode. After the addition of the solution the electrodes were finally dried for 1 hour at 110° C.

Eastman Commercial film was used in all work. This film recorded wave lengths down to 2400 Å. and was amply sensitive in the region used (2500 to 3400 Å.). The slit width employed was 0.009 cm. in all cases. The electrodes were preadjusted and the shutter was kept open, so that the exposure began as soon as the arc was started. Each exposure was made for exactly 1 minute from the time of striking the arc. It has been shown previously (3) that samples of this type and size are completely volatilized within 1 minute. Trials showed that, for the samples used in this investigation, this was indeed the case. The films were developed for 4 minutes at 20° C. in Eastman developer formula D72, using a fresh portion of developer for each film to ensure uniform development.

The density of the lines was measured with a simplified microdensitometer. A General Electric light-sensitive cell was connected in series with a Leeds & Northrup type R galvanometer, using a scale with radius of 1 meter. Illumination was furnished by a Westinghouse type H-3, 85-watt, high-intensity mercury vapor lamp. The linear source of light from this lamp was focused on the film by a lens to give an intensely illuminated strip, shorter than the line to be measured and nearly as narrow. The film was clamped to a horizontal carriage which was connected to a fine screw adjustment, by which the film might be moved accurately as small a distance as 0.0005 cm. (0.0002 inch). Directly below the film a defining slit, slightly narrower than the spectral lines, was placed to cut out extraneous light rays. The light-sensitive cell was placed approximately 3 cm. below this defining slit, enclosed in a light-tight box with the slit the only opening. The principal advantage of this arrangement lies in the high intensity of light passing through the line.

The blackness of each line was measured by obtaining the minimum deflection of the galvanometer and subtracting from the background reading (9). The background readings were fairly uniform, so that these values represent the line blackness with sufficient accuracy for the purpose at hand.

## Analysis of Films

A qualitative analysis of the films, using an iron comparison spectrum, showed calcium, magnesium, potassium, sodium, and phosphorus all present in large quantities; aluminum, boron, copper, iron, manganese, silicon, silver, titanium, and vanadium present in smaller quantities. None of the persistent lines for the other elements was detected.

Standard solutions for a rough quantitative analysis were made up as follows: A base-line solution was made containing sodium, potassium, calcium, magnesium, and phosphorus in the same proportions as were found in the egg ash by ordinary wet analysis. This solution was made from Baker's analyzed chemicals and contained the five elements used in the ratios: Na, 20.0; K, 19.2; Ca, 1.4; Mg, 1.5; and P, 1.75.

The concentration was adjusted so that the ratio numbers have also the number of grams of element in 100 grams of egg ash. The accuracy of the ratio numbers is shown by the fact that the base-line solution gave lines for these five elements which were almost exactly of the same intensities as the corresponding lines given by egg ash. Any impurities in the Baker's analyzed chemicals gave lines whose measured intensities set down limits on the sensitivity of the final analysis of the egg ash. These lower limits, were, in most cases,



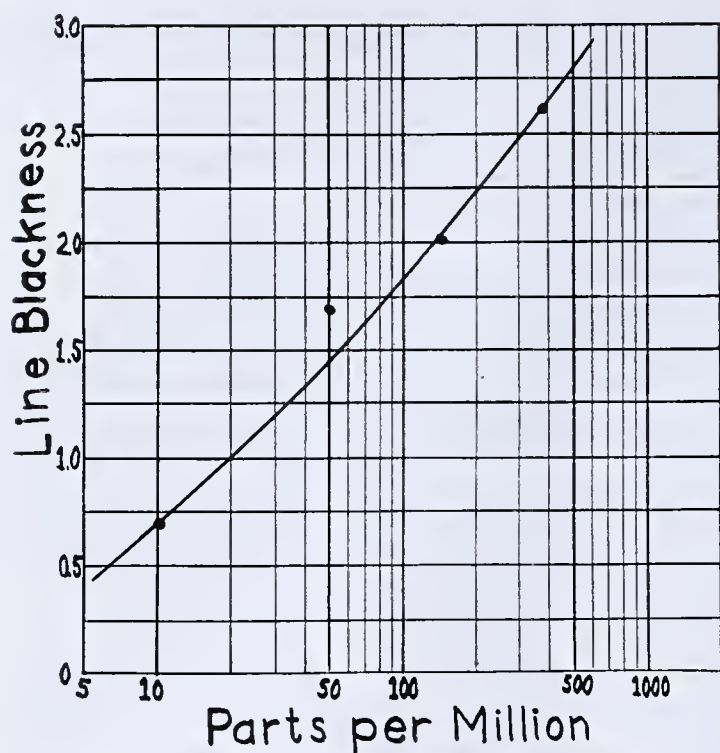


FIGURE 1. STANDARD CURVE FOR SILVER, 3280.67 Å.

sufficiently low for the purpose at hand. A rough quantitative analysis showed that the concentrations of the trace elements in nearly all the egg-ash samples were within the following ranges: iron, less than 100,000 parts per million of dry ash; manganese, vanadium, copper, silver, and titanium, less than 1000 parts per million of dry ash.

Using these results, a series of standard solutions was prepared from the general stock solution, adding the trace elements and concentrating to original volume. These standard solutions had the following concentrations of the trace elements: manganese, vanadium, copper, silver, titanium, and aluminum, 10, 20, 50, 150, 400, and 1000 p. p. m. on basis of dry ash; iron, 50, 150, 500, 1500, 5000, 10,000, 30,000, and 60,000 p. p. m. on basis of dry ash.

Spectra were made of these standards using conditions identical with those used for the egg-ash samples. Observation of the standard spectra indicated that the following lines were the most sensitive over the ranges of concentration being used: manganese, 2576.12 Å.; iron, unresolved doublet 3020.65 to 3021.08 Å.; vanadium, 3185.406 Å.; copper, 3273.97 Å.; silver, 3280.67 Å.; and titanium, 3349.04 Å.

The blackness of these lines was measured with the microdensitometer and expressed in arbitrary units from the scale of the galvanometer. These values were plotted as ordinates against parts per million of the element, using semilogarithmic paper. Only the most persistent line of aluminum, at 3961.54 Å., could be positively identified. However, it showed no gradation of intensity with decreasing concentration and could be used only in a qualitative way. The line of manganese at 2576.17 Å. is not sensitive below 50 p. p. m. but had to be used, since the most persistent line 4030.76 Å. appeared in the cyanogen bands and was therefore not suitable for analysis. Analysis was not made for boron and silicon, although their persistent lines were observed in the sample spectra. The spectra of the purified carbons

themselves gave these lines in varying concentrations; hence it was impossible to make analyses for these elements using graphite electrodes. Rough quantitative analyses were then made for the six elements by comparing the standard curves of Figures 1, 2, 3, and 4 with the blackness of the corresponding spectral lines from egg ash.

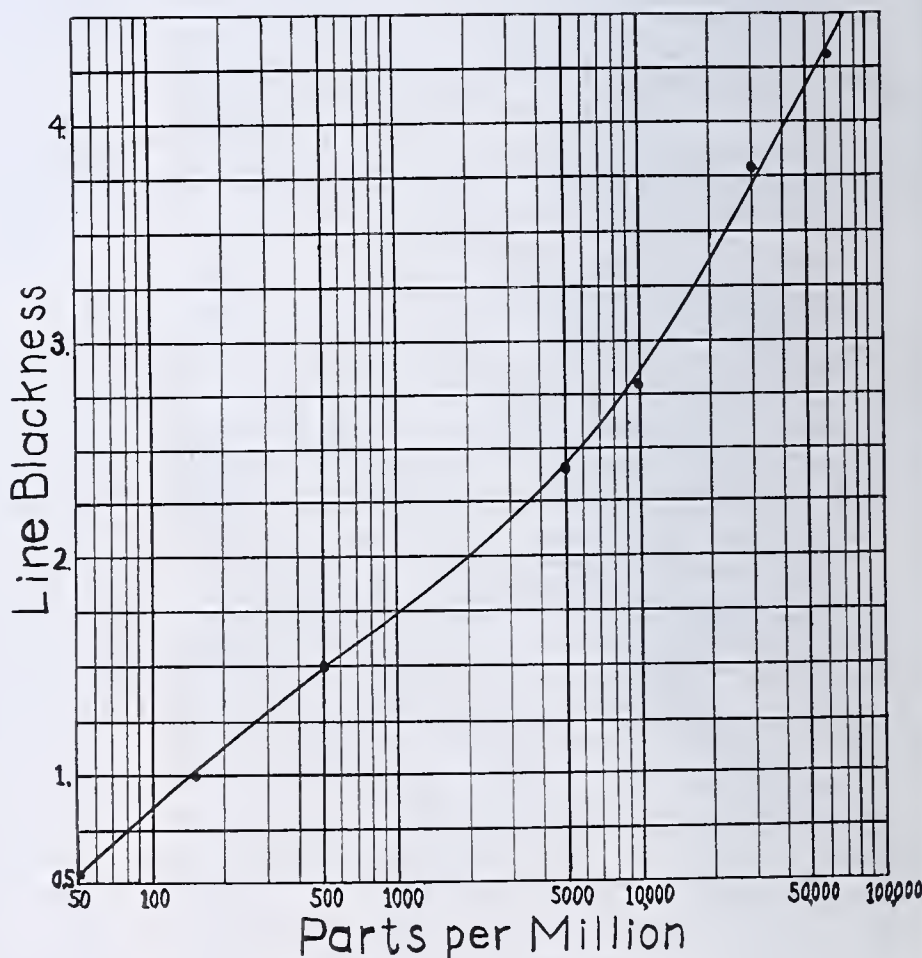
TABLE I. ANALYSES OF ASH OF EGG WHITES

Elements	Average of 10 Firm Whites P. p. m.	Average of 7 Watery Whites P. p. m.
Manganese	< 50	< 50
Iron	53	81
Vanadium	240	650
Copper	137	600
Silver	52	25
Titanium	84	850
Silicon	+	+
Aluminum	++	++
Phosphorus	+ or ++	+

It was shown by making repeated spectra from the same sample solution that the line-blackness measurements could be repeated with the following precision: silver, vanadium, titanium, and manganese to 0.1 division as shown on the graphs. Results could be duplicated to 0.2 division for iron.

### Results

Rough quantitative analyses for manganese, iron, vanadium, copper, silver, and titanium were made of the ash of separate whites and yolks of high- and low-viscosity eggs, and estimates were made as to the relative amounts of silicon, aluminum, and phosphorus. No difficulty was found in duplicating, within 15 per cent, successive analyses from a given sample. However, the analyses of supposedly similar successive samples varied many fold. Only average values for several apparently similar successive samples are given in Tables I to V.

FIGURE 2. STANDARD CURVE FOR IRON  
Unresolved doublet, 3020.65 to 3021.08 Å.



The symbols used in these tables to indicate the approximate amounts of these elements, estimated on the basis of spectra of standard solutions, are as follows:

Aluminum, + = 0 to 100 p. p. m.; ++ = 100 to 500 p. p. m.; +++ = 500 to 1000 p. p. m.  
Phosphorus, + = 0 to 1000 p. p. m.; ++ = 1000 to 5000 p. p. m.; +++ = 5000 to 20,000 p. p. m.

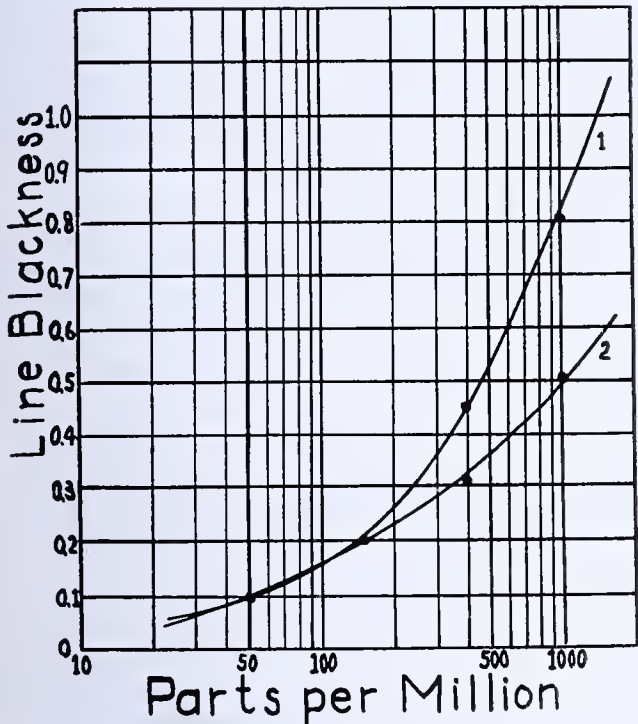


FIGURE 3. STANDARD CURVES  
1. Manganese, 2576.12 Å.  
2. Vanadium, 3185.406 Å.

Since silicon was present in the graphite electrodes used, no standards were made up with it present. Hence, it was impossible to give any estimate of amount present. However, the amounts of silicon present in the purified electrodes were in nearly every case much less than in any of the samples tested.

The egg whites analyzed were total whites and no separations were made of the white into its different divisions.

In addition to the analyses given in Tables I and II, analyses were made of the mineral content of the ash of the feed, and of the blood, liver, oviduct, and eggs from hens producing viscous and nonviscous eggs.

TABLE II. ANALYSES OF ASH OF EGG YOLKS		
Elements	Average of 2 Poor Yolks P. p. m.	Average of 6 Good Yolks P. p. m.
Manganese	< 50	50
Iron	2500	3000
Vanadium	200	200
Copper	130	200
Silver	2	4
Titanium	600	450
Silicon	+	+
Aluminum	++	++
Phosphorus	+++	+++

Other work was carried out trying to trace the presence of certain elements which were found in the feed ration through the egg and finally to the chick. The feeds used in these experiments had 40 parts per million of manganese added as manganese carbonate. The ash analyzed was approximately 10 per cent of the weight of the feed, hence 400 p. p. m. could be attributed to the addition of manganese car-

TABLE III. ANALYSES OF ASH OF EGGS AND ORGANS OF HENS LAYING VISCOUS EGGS AND OF THEIR FEED

Element	Feed P. p. m.	Blood P. p. m.	Liver P. p. m.	Oviduct P. p. m.	Egg Whites P. p. m.	Egg Yolks P. p. m.
Manganese	700	50	< 50	50	50	50
Iron	45,000	100,000	3500	150	50	150
Vanadium	1,400	150	150	150	150	400
Copper	160	160	400	1	250	1
Silver	6	1	1	None	1	1
Titanium	620	220	400	300	1400	400
Silicon	+++	++	+++	None	None	+
Aluminum	+	++	+++	++	++	++
Phosphorus	+++	++++	+++	++	+	++

TABLE IV. ANALYSES OF ASH OF EGGS AND ORGANS OF HENS LAYING NONVISCOUS EGGS AND OF THEIR FEED

Element	Feed P. p. m.	Blood P. p. m.	Liver P. p. m.	Oviduct P. p. m.	Egg Whites P. p. m.	Egg Yolks P. p. m.
Manganese	700	150	50	50	<50	<50
Iron	45,000	>100,000	>100,000	62	31	5000
Vanadium	1,400	2,000	150	None	150	400
Copper	160	10	800	1	90	250
Silver	6	30	1	1	1	1
Titanium	620	1,000	300	10	1800	1000
Silicon	+++	++	+	None	++	++
Aluminum	+	+	+++	++	++	+
Phosphorus	+++	++	++	++	+	+++

TABLE V. FEEDING PROJECT RESULTS

Elements	Feed 33 P. p. m.	Egg 4 P. p. m.	Chick 42 P. p. m.
Manganese	6,200	150	<50
Iron	22,000	31,000	40
Vanadium	400	700	50
Copper	10	160	None
Silver	1	10	None
Titanium	400	90	1400
Silicon	++++	+	+
Aluminum	++++	++	++
Phosphorus	++++	++	+

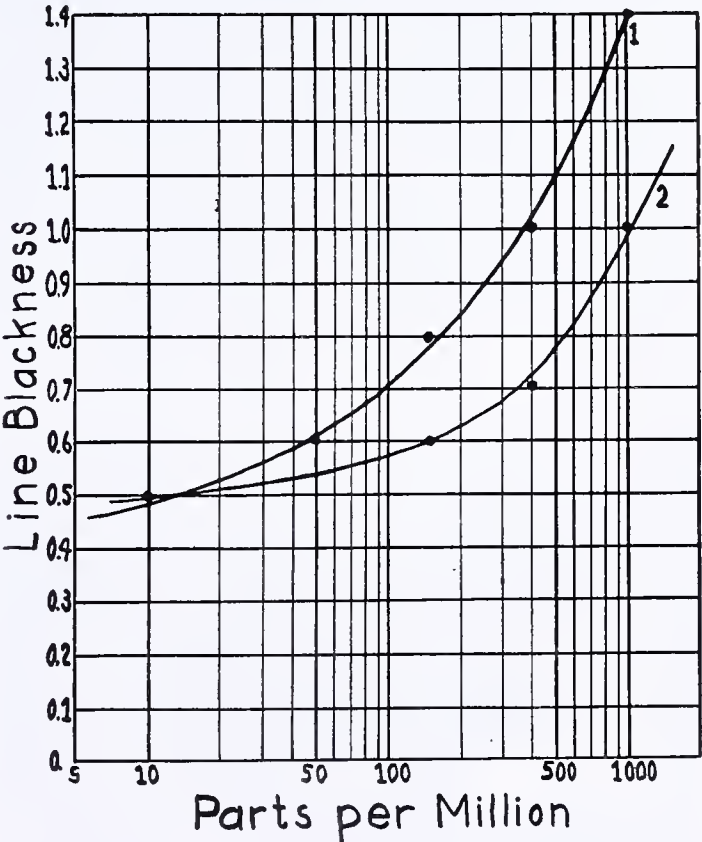


FIGURE 4. STANDARD CURVES  
1. Copper, 3273.97 Å.  
2. Titanium, 3349.04 Å.



bonate to the feed. Manganese was of special interest, since it has been shown that manganese present in the feed of poultry helps to control perosis (5).

Four such feeding projects were carried out and analyses run on the ash from the feed, egg, and chick. Nothing remarkable was observed from a biological standpoint. A typical analysis is given in Table V.

Analyses were made of still other rations, and also of eggs produced by hens fed these rations. However, no striking results were obtained and these analyses are not tabulated in this article.

### Summary

No direct correlation could be made between the quality of eggs and the content of trace elements present in them.

In a qualitative way the amounts of silicon and phosphorus were shown to be greater in the better quality eggs.

The precision of this rapid method of quantitative estimation, made on a relatively inexpensive replica-grating spectrograph, is not greater in extreme cases than 15 per cent.

The author wishes to thank W. J. Rudy of The Pennsylvania State College Poultry Department for the feeding of hens and ashing and preparation of samples; the Central Scientific Company of Chicago, Ill., for the loan of the spectrograph; and Wheeler P. Davey, research professor of physics and chemistry at The Pennsylvania State College, for his counsel and assistance.

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## Viscosity of Aniline between 20° and 100° C.

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The viscosity of "chemically pure aniline,"  $d_4^{20} = 1.0208 \pm 0.0003$ , was determined at 5° intervals from 20° to 100° C. with an accuracy of  $\pm 0.20$  to  $\pm 0.30$  per cent. The measured viscosities were compared with the results in the literature, the latter being in part confirmed and in part found doubtful. The author's results, comprising the most accurate and complete data available for the viscosity of aniline, make possible calibration at 100° C. with the same accuracy as has been accepted with water at 20° C. In comparison with water, aniline as a calibration liquid has the advantages of higher viscosity, much lower surface tension, and applicability at high temperatures.

THE capillaries and falling bodies of the viscometer are calibrated with a liquid, the viscosity of which is either known with definite accuracy or assumed to be standard. Accurate knowledge of the absolute viscosity is preferable to the acceptance of a relative standard. The viscosity,  $\eta$ , divided by the time,  $t$ , required for the flow of a certain quantity of liquid or for the travel of the falling body, gives the calibration value,  $k = \eta/t$ , which may be either a constant or a variable. Inasmuch as with many viscometers, especially the metal ones,  $k$  varies with the temperature, it is desirable to know the exact viscosity of the standard liquid at the higher temperatures.

It often happens in practice that exact information is not available regarding the viscosity of a liquid, which otherwise would be suitable for a standard. Naturally the choice of a standard depends upon the accuracy required; at the present

time the correct viscosity in c. g. s. units of no liquid is known with greater accuracy than about  $\pm 0.2$  per cent. This is true for water at 20° C., and at higher temperatures the accuracy is far less. Since water has a very low viscosity, it is not suitable for the calibration of apparatus intended for the measurement of high viscosities. Although viscous oils have been measured very accurately, such standards are obtainable only at a high price; moreover, the viscosity of the oils increases about 0.2 to 1 per cent per year, so that they are satisfactory only for a limited time as standards for accurate calibration.

### Aniline as Calibration Liquid

Unfortunately, there are no chemically pure stable liquids that have a viscosity approximating that of automobile oil. However, aniline, which is obtainable commercially in pure form at relatively low cost, facilitates the selection of suitable standard liquids. The viscosity of aniline is about four times that of water. Although this difference is not great, one can conveniently measure light oil with a capillary calibrated with aniline, and then utilize this light oil as a standard for measuring the viscosity of viscous oils.

The viscosity curve of aniline was determined in some detail by Bingham, van Klooster, and Kleinspehn (3) in 1919 and by Erk (4) in 1926. The results of other authors were obtained for the most part at room temperature or slightly lower. The viscosity curve is highly important, because, as already pointed out, the constants of many viscometers change with the temperature. The determination of the viscometer constant at room temperature and at only one viscosity is insufficient for many practical problems and entirely untrustworthy for scientific purposes.

### Viscosity Measurements

With the aid of a Steiner falling-body viscometer, Type MLD, the author, using two bodies, measured the dynamic viscosity (centipoises) of aniline at 20° C. Commercial chemically pure aniline, which had a very slight yellow



color, was vacuum-distilled for use, although the viscosity was not altered by the distillation. As measured with a pycnometer its density with respect to water at 4° C. was 1.0208 ± 0.0003 at 20° C. and 0.9527 ± 0.0003 at 100° C. The thermal expansion of the glass was taken into consideration, but the buoyancy of the air was neglected. These figures agree with the results given in the literature. Thus, the published values for 20° C. are given as 1.0203 in Landolt-Börnstein (8), 1.0208 by Erk (5), and 1.0217 in the International Critical Tables (7). The latter give 0.9514 for the density at 100° C. The author's result is less than the I. C. T. value at 20° C. and greater than the I. C. T. value at 100° C., the difference being about 0.001 in each case.

The viscosity at 20° C. was determined under the following conditions:

- 1. The temperature was read to within ±0.01° C.
- 2. The uncertainty of the corrected thermometer reading amounted to ±0.01° C., which corresponds to an uncertainty in the viscosity of ±0.04 per cent.
- 3. The time was measured to ± 0.1 second. Measurements were made for a series of temperatures both below and above 20° C., the points were plotted, and the measurements were repeated twice with fresh portions of aniline. Two observers kept the time with three stop watches. Deviations greater than 0.5 per cent were excluded, and the time interval was accurate to ± 0.03 per cent.

The accuracy of the constant, which multiplied by the time gives the viscosity, remains to be estimated. To this end the viscosities between 15° and 18° C. were determined at the same temperatures at which Erk's measurements were made with the fundamental viscometer. The two sets of results are compared in Table I.

TABLE I. COMPARISON OF VISCOSITY MEASUREMENTS BETWEEN 15° AND 18° C.

Temperature ° C.	Viscosity Found by Erk Centipoises	Steiner Centipoises	Deviation, δ %	(100δ) <sup>2</sup>
15.35	5.20	5.214	0.27	729
16.31	5.01	5.025	0.30	900
16.33	5.02	5.021	0.02	4
16.48	4.93	4.992	1.25	...
16.60	4.97	4.969	0.02	4
17.28	4.85	4.845	0.10	100
17.49	4.84	4.808	0.67	4489
Σ (100δ) <sup>2</sup> = 6126				

The data agree very well with the exception of the results at 16.48° C., where the deviation of 1.25 per cent is to be attributed to an error in Erk's result. According to the method of least squares, the probable deviation between the two sets of measurements is ±2/3 [0.6126/(6 × 5)]<sup>1/2</sup> = ±0.095 per cent.

The author's results at 20° C. varied between 4.397 and 4.402, and the mean of 6 measurements was 4.400 centipoises. Erk's equation for the viscosity curve of aniline yields a value of 4.36 centipoises at 20° C.; this equation is, however, not reliable. Later in Landolt-Börnstein (9), Erk gave the viscosity as 4.40 centipoises. Bingham, van Klooster, and Kleinspehn found a value of 4.429 centipoises at this temperature, which is 0.66 per cent higher than the author's result. This discrepancy is discussed later.

The possible error in the author's results, comprising uncertainties in the constant *k* (±0.10 per cent), the temperature (±0.04 per cent), and the time (±0.03 per cent), amounts to ±0.17 per cent. Considering the uncertainty arising from possible impurities in the aniline, it can be said that the uncertainty in the value 4.400 centipoises is probably ±0.20, or at most ±0.25 per cent.

The foregoing result (4.400 centipoises) for the viscosity of aniline was taken as the standard for the calibration of two

other Steiner viscometers, type MRJ, provided with thermometers whose corrected readings were accurate to ±0.1° C. The viscosity of aniline was determined at 5° intervals between 20° and 100° C. with each instrument. The measurement at each temperature comprised five fillings of each viscometer, so that the results (Table II) represent the average of 10 determinations of the time.

TABLE II. VISCOSITY OF ANILINE AT 20° TO 100° C.

Temperature ° C.	Viscosity Steiner Centipoises	Found by Bingham <i>et al.</i> Centipoises	Deviation, δ %	(100δ) <sup>2</sup>	Accuracy of Steiner's Result ± %
20	4.400	4.429	0.66	4356	0.20
25	3.770	3.781	0.29	841	
30	3.218	3.221	0.09	81	
35	2.783	2.826	1.55	Not calcd.	
40	2.432	...	...	...	0.25
45	2.150	2.158	0.37	1369	
50	1.919	...	...	...	
55	1.726	...	...	...	
60	1.557	1.553	0.26	676	0.20
65	1.415	...	...	...	
70	1.296	...	...	...	
75	1.190	...	...	...	
80	1.098	1.094	0.37	1369	0.20
85	1.018	...	...	...	
90	0.9455	...	...	...	
95	0.8817	...	...	...	
98	0.840	0.838	0.24	576	0.20
100	0.8284	...	...	...	
Σ(100δ) <sup>2</sup> = 9268					

Bingham *et al.* determined the viscosity of aniline at certain temperatures up to 100° C. For comparison their results are also given in Table II. With the exception of the result at 35° C. the deviations are relatively small. The next largest deviation is at 20° C. from which it is concluded that the result by Bingham *et al.* for this temperature is high. Using the same procedure in the discussion of Table I for determining the agreement between the sets of data, the method of least squares gives ±2/3 [0.9268/(7 × 6)]<sup>1/2</sup> = ±0.10 per cent. This noteworthy result is attributable to the fact that the figure used for time was the average of ten measurements and to the relatively large number of comparison points.

The author's measurements were facilitated by the fact that only 6 cc. of liquid are required for a filling and that a set of measurements for the entire temperature range can be made with the single filling. Liquid used for measurements at 100° C. was always brought to 20° to 40° C. before it was emptied, and a turbidity was observed in only one instance.

The experimental results obtained by Erk in the neighborhood of 80° and 100° C. are apparently very accurate, whereas those at lower temperatures, around 30°, 50°, and 60° C., show wide deviations. This is probably due to Erk's use of different methods of measurement for the two temperature ranges. Since Erk pointed out the lack of precision in his measurements in the range 30° to 60° C., it is not necessary to give further attention to it here.

Erk (6) also published an equation for the viscosity of aniline as a function of temperature:

log (100η) = -1.1485 (t - 85.26)/(t + 97.1)

in which η is in poises and *t* is in degrees Centigrade. The values obtained with the aid of this equation are higher than the most recent results for the viscosity of aniline by 0.87 per cent at 20°, 1.60 per cent at 60°, and 0.36 per cent at 100° C. When log η is plotted against the reciprocal of the absolute temperature—a treatment that on the basis of certain theoretical considerations seems profitable—the result is a curved instead of a straight line.

With one exception (Table II) the results of Bingham *et al.* at temperatures above 25° C. and with a single exception (Table I) the results of Erk at room temperatures and in the neighborhood of 80° and 100° C. are, in the author's opinion, accurate figures for the viscosity of aniline. In so far as the



literature available to the author shows, his results are the most accurate and complete data available for temperatures between 20° and 100° C. The average accuracy of the results in Table II is about  $\pm 0.25$  centipoise, and the uncertainty of any one result is only as great as is caused by an uncertainty of  $\pm 0.1^\circ$  C. in the temperature measurement, which is at least  $\pm 0.20$  per cent. The accuracy at 20° C. is obvious from the results in Table I.

There remains the question as to how the results would be affected if aniline was not absolutely pure. The viscosity of a sample of aniline that was darker in color and had a density greater by 0.003 than the product used in the viscosity measurements was observed to be 0.6 per cent higher than that of the purified material. Another sample with the same density as used in the viscosity measurements had the same viscosity. Aniline with a density of 1.014 showed a viscosity of 4.32 centipoises; accordingly, a density change of  $\pm 0.0003$  corresponds to a  $\pm 0.07$  per cent change in the viscosity. Since an uncertainty of this order is acceptable, the question was not investigated further.

Aniline must be distilled for viscosity measurements, but this is also true of water. When it is protected from light and the atmosphere, aniline can be kept 2 months without change. Aniline vapor attacks paper. The vapor is poisonous only in concentrations higher than those likely to occur incident to viscosity measurements—at least, the author noticed no ill effects. Furthermore, the viscosity of aniline is not especially high. However, in stepwise standardization beginning directly with water, the first step is most uncertain as a consequence of turbulence and surface tension. A viscosity of 4.4 centipoises is sufficiently large to permit convenient standardization of an oil with a viscosity of about 25 centipoises. The latter can then be used for the calibration and control of instruments.

### Advantages of Aniline

One great advantage of aniline lies in the fact that its surface tension is only slightly larger than that of lubricating oil. Barr (1) has pointed out the relatively large effect of surface

tension—for example, with capillaries of range 1 of the British Standard BESA-188, an error of 0.8 per cent arises from this cause on changing from water to oil. It is, however, possible to eliminate the influence of surface tension in capillary apparatus. Surface tension had no effect on the author's measurements, because active surfaces are not present in the falling-body apparatus.

Aniline is far more suitable than water for measurements at high temperatures. It can be used in a closed apparatus, such as is provided in the Steiner viscometer, at 100° C. and above without danger of evaporation.

Furthermore, according to Bingham (2), the uncertainty in the present accepted values for the viscosity of water amounts to 0.5 per cent—that is,  $\pm 0.25$  per cent. Thus, aniline passes the test in this respect. Whereas water can be employed for calibrations of the required accuracy only at 20° C., distilled aniline having a density of 1.0208 may, with the aid of the results given in this paper, be used for calibration at temperatures from 20° to 100° C. In view of the fact that the constants of many viscometers vary with the temperature, and for other reasons, the ability to calibrate instruments at the higher temperatures appears to be extremely important.

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## A Liquid Bath Melting Point Apparatus

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THE melting point apparatus represented in Figure 1 combines a high degree of general convenience, moderate rapidity, and a very satisfactory level of accuracy. The design of the outfit and the dimensions indicated are such as to avoid the disadvantages of a large liquid bath, and also difficulties in uniform heat distribution and in heat regulation as the melting point is approached, which may be encountered in the use of very small baths. If strongly made of Pyrex or similar glass, the apparatus is substantial and may be regarded as no more fragile than other glass apparatus. Several outfits of this type have been in use for a number of years, one in the hands of students, without breakage.

The capacity of bulb A is about 100 cc. The cap, H, seated in a ground joint, has three tubulures, one for the melting point thermometer, F, one for the auxiliary thermometer, G, and the third for the wiper, E. The profile of the apparatus is an unbroken vertical line, with only a convex curvature along the vertical axis. This produces a noticeable horizontal magnification of

objects within the bath, but no distortion. The "bridge," B, is attached at two points near the base of the neck and supports the small horizontal platform, D. In depressions a, b, b are seated, respectively, the melting point thermometer and the melting point tubes. The support, D, and the tubulures mentioned are so placed with respect to each other that the thermometer is parallel with the front wall and about 5 mm. from it, and that the melting point tubes, inserted through the oblique tubulures shown in Figure 1, are seated beside and slightly forward of the bulb of the thermometer, in such position that the rear illumination of the charge in the melting point tube is unimpaired.

When the bath is at room temperature the immersion of the thermometer is about 20 mm. The melting point tubes are about 7 cm. long. The screw-type stirrer, C, extends obliquely through opening O and between the two supporting arms of B to a point near the bottom of the bath and directly beneath platform D, and is rotated by a small disk motor with rheostat control. The wiper, E, is made from two pipe cleaners joined by twisting two ends together, a free end being then bent into a loop of such diameter that manipulation of the wiper will clear the glass wall of drops or liquid film which decreases the visibility of the thermometer. The apparatus is seated in a 4-cm. circular hole in an



asbestos board (not shown), and is held in place by means of a clamp attached at *O*. The gas supply is regulated by use of a glass stopcock with an elongated handle.

The melting point thermometer is of the enclosed-scale type, and has the general dimensions of the familiar Anschütz thermometers. It is calibrated for total immersion, with a range from 30° to 300° C. in 1° intervals. The over-all length is 180 mm., the length to the 300° mark is 120 mm., and the diameter is 5 mm. The bulb is 5 mm. high and 5 mm. in diameter at the top, tapering to 3 mm. at the end. The entire scale of the thermometer is within the apparatus. The divisions of the scale are too small to be read satisfactorily with the unaided eye, but by use of the buret reader, *M*, readings to 0.1° can be made with ease. A collar of rubber tubing (not shown), which makes contact with the tubulure of cap *H*, assists in keeping the thermometer in position. A set of short-scale thermometers may be used instead of the single thermometer described.

TABLE I. MELTING POINT DATA

Substance	Melting Point Observed	<i>t</i> <sup>a</sup>	<i>N</i> <sup>a</sup>	Stem Correction	Calibration Correction	Melting Point Corrected	Accepted Melting Point
Benzoic acid	122.2	76	72	+0.5	-1.1	121.6	...
	122.5	86	72	+0.4	-1.1	121.8	121.7
Benzanilide	163.0	95	113	+1.2	-1.5	162.7	...
	163.2	100	113	+1.1	-1.5	162.8	163
Carbazole	242.2	132	182	+3.3	0.0	245.5	...
	242.4	135	182	3.2	...	245.6	...
	242.4	134	182	3.3	...	245.7	...
	242.7	138	183	3.1	...	245.8	...
	242.0	135	182	3.2	...	245.2	...
Av.						245.6	244.8

<sup>a</sup> Formula used: Correction =  $N(t - t')0.000154$ .

The auxiliary thermometer, *G*, includes the range 30° to 180° C. on a scale which occupies the lower 55 mm. of the stem—i. e., which is wholly within the apparatus when the thermometer is in the topmost position to which it need be raised in use. This thermometer has a small bulb and is employed in the usual manner for determination of the emergent stem corrections to be applied to the readings of the melting point thermometer. The auxiliary thermometer is held at any desired level by means of a collar of rubber tubing which rests on the tubulure of *H*.

The biconvex lens, *N*, is dispensable, but is desirable as it improves the visibility of the melting point phenomena. The telescope, *M*, and the lens, *N*, are supported by clamps on a small ring stand. A racking device would be an added convenience.

For the trials whose results appear in Table I, thermometer *F* was calibrated by direct comparison with Anschütz thermometers tested by the Bureau of Standards. The melting point tube was in each case introduced when the temperature of the bath was 10° below the melting point of the substance, with the thermometer showing a rise in temperature of 2° per minute. The melting point was taken as the temperature at which a liquid meniscus first appeared. The data recorded in Table I indicate the magnitudes of the stem corrections at several temperatures, the precision of the results, and their accuracy, as determined with several compounds purified by repeated crystallizations.

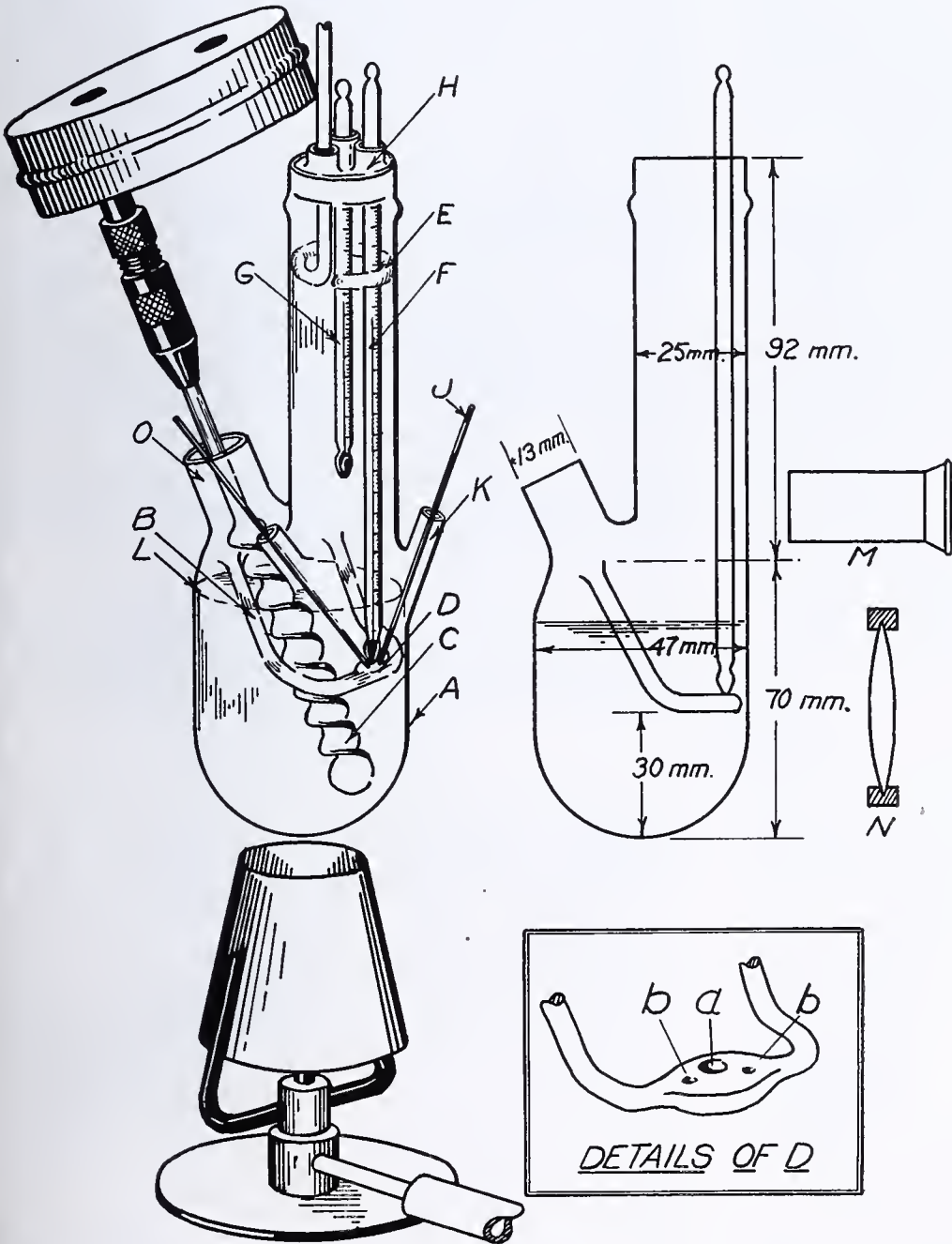


FIGURE 1. MELTING POINT APPARATUS



# Detection of Small Amounts of Phenolphthalein

## In the Presence of Emodin and of Chrysophanic Acid

EUGENIA H. MAEHLING, College of Physicians and Surgeons, Columbia University, New York, N. Y.

WHEN phenolphthalein is the main active principle in medicinal preparations, its detection and determination are as a rule readily accomplished (1, 13). When, however, it is accompanied by certain laxative plant products, such as cascara, aloes, rhubarb, senna, or frangula, which contain polyhydroxyanthraquinones, its detection may offer considerable difficulties due to the similarity of their chemical behavior (3, 7).

These anthraquinone derivatives—namely, frangula-emodin (also present in cascara sagrada and in rhubarb), aloe-emodin (also present in senna), and particularly chrysophanic acid (chrysophanol, 2)—show in alkaline solution a variety of rather stable colors (18, 19), from cherry-red to purplish red, sometimes indistinguishable from that of phenolphthalein, the presence of which may thus be obscured. On acidification such solutions turn yellow or yellowish brown; phenolphthalein is colorless under these conditions.

The similarity of color reactions, including those given with concentrated sulfuric acid (11, 16), and the difficulty in separating the anthraquinone derivatives from phenolphthalein by means of organic solvents (19), made desirable an analytical method which would be characteristic for phenolphthalein and negative for the polyhydroxyanthraquinones in question, and thus permit with certainty the identification of phenolphthalein in some medicinal preparations (4).

It was found that the purplish red solution of phenolphthalein in potassium hydroxide when treated with an excess of hydrogen peroxide undergoes a gradual decoloration, resulting from oxidative cleavage. When the colorless alkaline solution is cooled, acidified with dilute sulfuric acid, and extracted with ether, phthalic acid can be isolated from the ethereal extract and identified by its melting point and its ability to yield fluorescein when heated with resorcinol.

When the oxidation by hydrogen peroxide in alkaline solution was carried out upon certain plant products such as rhubarb powder, cascara sagrada, and powdered aloes, to which known amounts of phenolphthalein had been added, oxidation products were obtained which also gave fluorescent solutions on heating with resorcinol under suitable conditions. Since some organic acids like oxalic, malic, citric, and succinic respond in this way, all materials to be analyzed must uniformly first be treated with an excess of sodium bicarbonate solution, and the phenolphthalein extracted with ether. This procedure not only achieves the separation of phenolphthalein and the polyhydroxyanthraquinones from the organic acids and other water-soluble substances, including some anthraglucosides possibly present, but may at the same time reveal the absence of emodin and of chrysophanic acid in samples from which the ethereal extracts prove to be colorless.

Oxidation experiments carried out upon authentic samples of rhubarb, senna, aloes, and cascara sagrada unmixed with phenolphthalein gave uniformly negative results in the test for phthalic acid. Experiments with commercial chrysarobin powder were also negative (5, 6, 17).

The absence of phthalic acid in these oxidation products can well be explained by the following considerations: The anthraquinone derivatives—namely, frangula-emodin, 1,8,6-trihydroxy-3-methylanthraquinone, aloe-emodin, 1,8-dihydroxy-3-oxymethylanthraquinone, and chrysophanic acid, 1,8-dihydroxy-3-methylanthraquinone—occurring in the above-mentioned plant products are related to chrysazin (1,8-

dihydroxyanthraquinone, 10, 12), which on oxidation does not yield phthalic acid (8).

Chrysazin (Istizin) has also laxative properties.

### Procedure

A suspension of 0.5 to 1 gram of the powdered sample in 20 cc. of a freshly prepared solution of sodium bicarbonate is shaken in a separatory funnel three times with ether, using 25 cc. for the first and 15 cc. for each subsequent extraction. The combined ethereal extracts are washed and evaporated to dryness.

The residue, containing phenolphthalein and the anthraquinone derivatives originally present, is dissolved in 20 cc. of 10 per cent potassium hydroxide and the red to purple solution is oxidized by successive additions of 30 per cent hydrogen peroxide, preferably in a beaker or a porcelain casserole, heating gently over a low flame. An Erlenmeyer flask should not be used for this process, because of foaming and a tendency of the alkaline solution to creep.

The solution is allowed to settle in the cold. A purplish sediment of alkali salts of anthraquinone derivatives (3, 15), if present, is removed, and the alkaline solution is cooled with ice and acidified with an excess of dilute sulfuric acid.

Effervescence and a change of color to colorless or yellow take place. The solution is extracted with three successive portions of ether, using 20, 15, and 15 cc., respectively. The combined ethereal extracts are washed and evaporated first in a casserole to a small volume at room temperature and finally to dryness in a Pyrex tube surrounded with water at about 60° C. The residue in the test tube is heated with an excess of resorcinol in a metal bath at 180° to 200° C. for 20 minutes, or at boiling temperature for 5 minutes over a small flame. No condensing agent is used (9, 14).

The resulting melt is dissolved in about 5 cc. of potassium hydroxide and diluted with water. According to the quantity of phenolphthalein present in the original sample, a more or less pronounced green fluorescence will be observed.

The presence of 5 to 10 gamma of phenolphthalein in the original mixture can be detected by this procedure.

Cascara sagrada tablets to which succinic acid and oxalic acid had been added gave negative fluorescence tests.

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# A Glass Vapor-Density Balance

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VAPOR-density balances are very useful in connection with apparatus used for the study of gases. A very satisfactory design is shown in Figure 1. It is made entirely of Pyrex glass, has a vapor jacket to maintain constant temperature during measurements, and has been found to be as sensitive as the pressure can be read on an ordinary mercury manometer.

The beam can be adjusted for center of gravity by careful bending, and the balance can be adjusted by carefully pulling off or adding small pieces of glass. If this is done at ordinary laboratory temperatures and pressures, the balance when assembled will balance in pure oxygen at about atmospheric pressure, when the vapor of boiling acetone is used in the jacket. The increase in temperature approximately com-

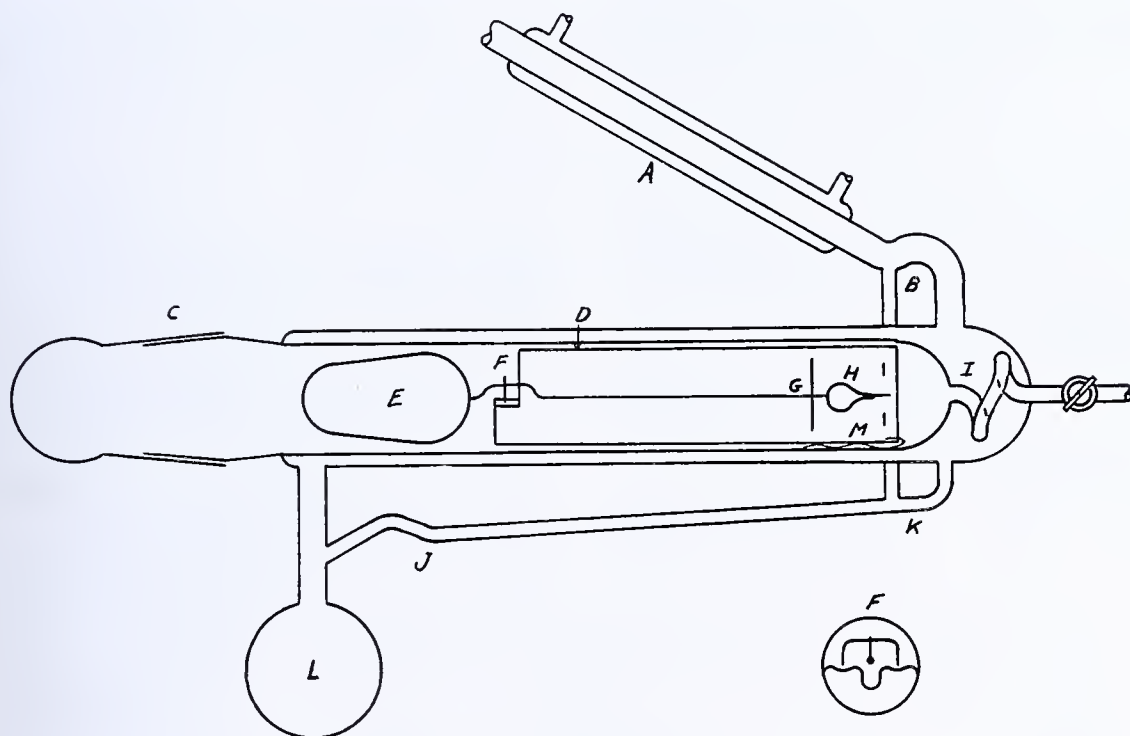


FIGURE 1. DIAGRAM OF GLASS VAPOR-DENSITY BALANCE

- |                           |                 |                |
|---------------------------|-----------------|----------------|
| A. Water-cooled condenser | F. Bearing      | K. Return tube |
| B. Trap                   | G. Cross rod    | L. Flask       |
| C. Ground joint           | H. Counterpoise | M. Springs     |
| D. Support tube           | I. Spiral       |                |
| E. Closed bulb            | J. Liquid trap  |                |

The beam is made of rod about 1 mm. in diameter, and is about 17 cm. long. At one end is a closed bulb,  $E$ , which is as thin as it can be made and yet have sufficient mechanical strength. It tapers toward the far end, so that it does not strike the containing wall during swings. The bearing at  $F$  is made of thin rod which terminates in two sharp but fire-polished points. The cross rod,  $G$ , serves to stop the swings when its ends strike the wall of the support tube and prevents the bulb with its greater surface from making contact with the wall. The counterpoise,  $H$ , terminates in a pointer.

The support tube, *D*, about 35 mm. in outside diameter, makes a close but not tight fit in the inner tube, and is prevented from rotating by springs of flat metal, *M*, between it and the tube wall. The support is made by tearing a slot in the tube more than half way around and about 1 cm. from the end and shaping with carbon rods. It contains shallow depressions in which rest the bearing points. The inner tube, about 38 mm. in outside diameter, terminates at one end in the large ground joint, *C*, and at the other in a short spiral, *I*, which extends through the end of the outer tube and becomes the connecting tube to whatever apparatus the balance is attached. The outer tube, about 51 mm. in outside diameter, is connected on the lower side to the flask, *L*, by means of two tubes, one for vapor and a return tube, *K*, for liquid, and on the upper side to a water-cooled condenser, *A*. A shallow trap, *B*, and drain return the condensed liquid without its flowing back into the jacket. *J* is a liquid trap.

pensates for the increase in density of oxygen over air. It is desirable to cover the outer tube with a thin coating of asbestos paper for heat insulation except for places at which to observe the pointer and bearings. A telescope with cross hairs is convenient for observing the pointer. The center of gravity can be adjusted so that a difference of pressure of 1 cm. of mercury at the balance point will cause the beam to change from its extreme upper position to its extreme lower position. This gives a precision of readings comparable with the precision with which a mercury manometer can be read, or in the region of 500-mm. pressure an accuracy of 0.2 per cent.

This device has been found very useful in determining the molecular weights of unknown gases, and in following the course of distillation of a mixture containing a homologous series of compounds having a number of isomers. Cuts can be made in the distillation at constant molecular weight rather than at constant temperature. This balance has been found to retain its calibration over periods of months.

RECEIVED July 26, 1938.





# The University of Delaware Chemical Laboratory

ALBERT S. EASTMAN, University of Delaware, Newark, Del.

THE new chemical laboratory of the University of Delaware, Newark, Del., the gift of H. Fletcher Brown of Wilmington, was dedicated on October 15 and 16, 1937. The building, which is of colonial design in harmony with the other colonial brick buildings of the university, was erected by the Ballinger Company of Philadelphia in coöperation with Charles Z. Klauder, architect, of Philadelphia, and Robert P. Schoenijahn, engineer, of Wilmington.

The size, shape, and interior arrangement are shown in the three accompanying floor plans. The nearly square building makes possible very economical construction. The building contains 680,000 cubic feet, on which building costs are com-

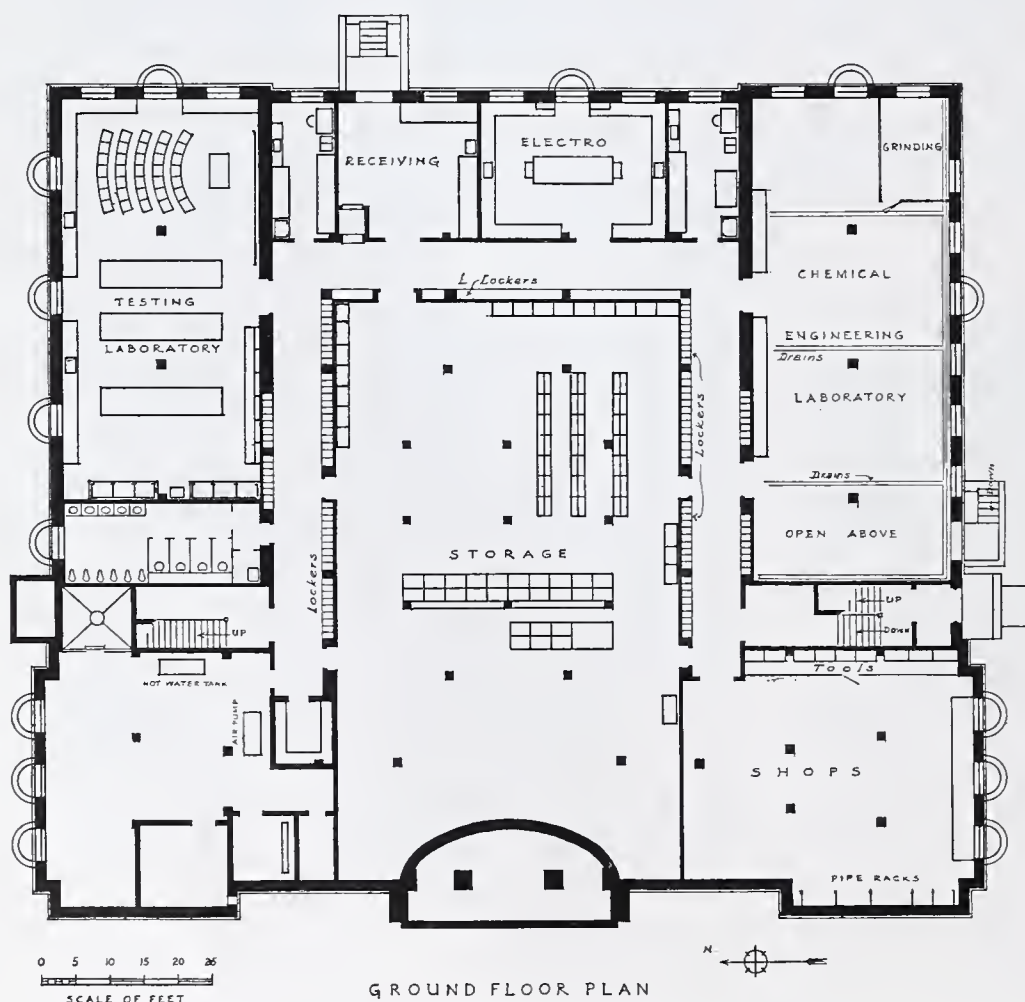
puted, and cost \$346,970 or 51 cents per cubic foot—an extremely low cost which was reached without sacrifice of utility, appearance, or durability. This includes plumbing, heating and ventilating, electrical work, and laboratory tables, but does not include movable furniture, portable laboratory equipment, nor architect's and engineer's fees. In addition \$22,000 has been set aside for laboratory equipment, mostly in the chemical engineering laboratory, and for additions to the department library, which has shelf room for two thousand books.

The interior walls, except in the entrance hall and the library, are of 5 × 12 Natco hollow unglazed tile of a light buff color. They have a substantial look and at the same time a very trim and pleasing appearance. The entrance hall and library have plaster walls decorated to match. The hall or lobby has several built-in, illuminated aluminum show cases, with glass shelves, for the exhibition of material of scientific or technical interest.

The floors are of brick in the entrance hall, linoleum in the library, and concrete in the chemical engineering laboratory. In the laboratories, class rooms, and halls the floors have a special hard-finish asphaltum top, about 1 inch thick, applied hot, over the concrete. Acoustic ceilings are used in the library, class rooms, and lecture room.

The building has more than the usual number of service outlets, and the plumbing, heating and ventilating, laboratory furniture, chairs, and fixtures are of the best quality and workmanship obtainable. Every effort was made to have the laboratory satisfactory in every detail.

The laboratory furniture is of steel, with soapstone desk tops and sinks, and is finished in olive-green to match the steel office furniture. All the shelves, drawers, and lockers





in the laboratories and stock rooms have been lined with Sisal-kraft tar paper, bent up at the sides and ends to form a shallow, water-proof tray. The bottom of this tray is covered with a sheet of thick gray lining paper, which is absorbent and may be easily replaced. The tar paper may be purchased of any dealer in roofing paper, and the lining paper of the Eaton-Dikeman Company. The paper linings were suggested by Dr. Foulk of Princeton University.

Each desk in use by students beyond the freshman year has a long drawer for burets and condensers, as well as a pencil tray in each large drawer. The shelf in the cupboard below does not extend all the way to the front, thus providing space for tall bottles and ring stands. All laboratory desks, and the lockers on the ground floor, are provided with master-keyed combination padlocks.

A feature of the building is the large amount of storage available. All the space under the lecture room and lobby is for rough storage, the laboratories are well provided with shelving and cabinets for reagents and apparatus, the preparation room is larger than is usual, and one large centrally located stock room serves the building. The arrangement makes it convenient for one man to look after the stock room, preparation room, and lecture table. There are a call bell and a mail slot at the delivery window.

Both classrooms and laboratories are provided with slate blackboards, set in aluminum frames with aluminum chalk trays. In each case, a 2-foot section is of cork board for use as a bulletin board. Every blackboard has sliding hooks at the top for hanging charts and drawings, and also a strip of cork board, 1-inch wide for use with thumb tacks, set into the top of the frame.

The distilled water system is of aluminum. Streamline copper pipe and solder-type cast-copper fittings with special valves are used on all cold, hot, and circulation water piping.

The chemical engineering laboratory is 71 × 28 feet with windows on two sides. One end is two stories high, to provide for the two-stage evaporator, distillation column, absorption tower, and other relatively tall equipment. The balcony or gallery is for gravity flow experiments, and a traveling crane is located over the balcony and two-story portion. Numerous outlets for high-pressure steam, air, gas, hot and cold water, electric power, direct current, etc., are located at the columns and in each bay in order to provide flexibility in use.

Two of the offices have private laboratories attached, but twelve other rooms are intended to serve as combination offices and private laboratories. The larger of these have two laboratory tables, fitted with gas, air, water, steam, suction, alternating and direct current, a hood, office desk, two chairs, bookcase, filing cabinet, and wardrobe.

The building was planned to be run by a staff consisting of two janitors, one mechanic, one stock-room man, and one secretary-librarian. During one year of use this has proved to be satisfactory.

Ventilation

The main laboratories and all research rooms are connected to systems of mechanical exhaust ventilation. There are five exhaust systems, each having sheet-lead ducts with separate branches and risers leading from the hoods, and also general exhaust ducts with outlets at both floor and ceiling to remove both heavy and light gases from the room. In general the ducts extend up through the building, within the double partitions of the corridor walls, into the attic space, where they connect to the main horizontal ducts, going to their respective fans. The fans have sheet-lead discharge ducts extending into lead-lined masonry vent chimneys.

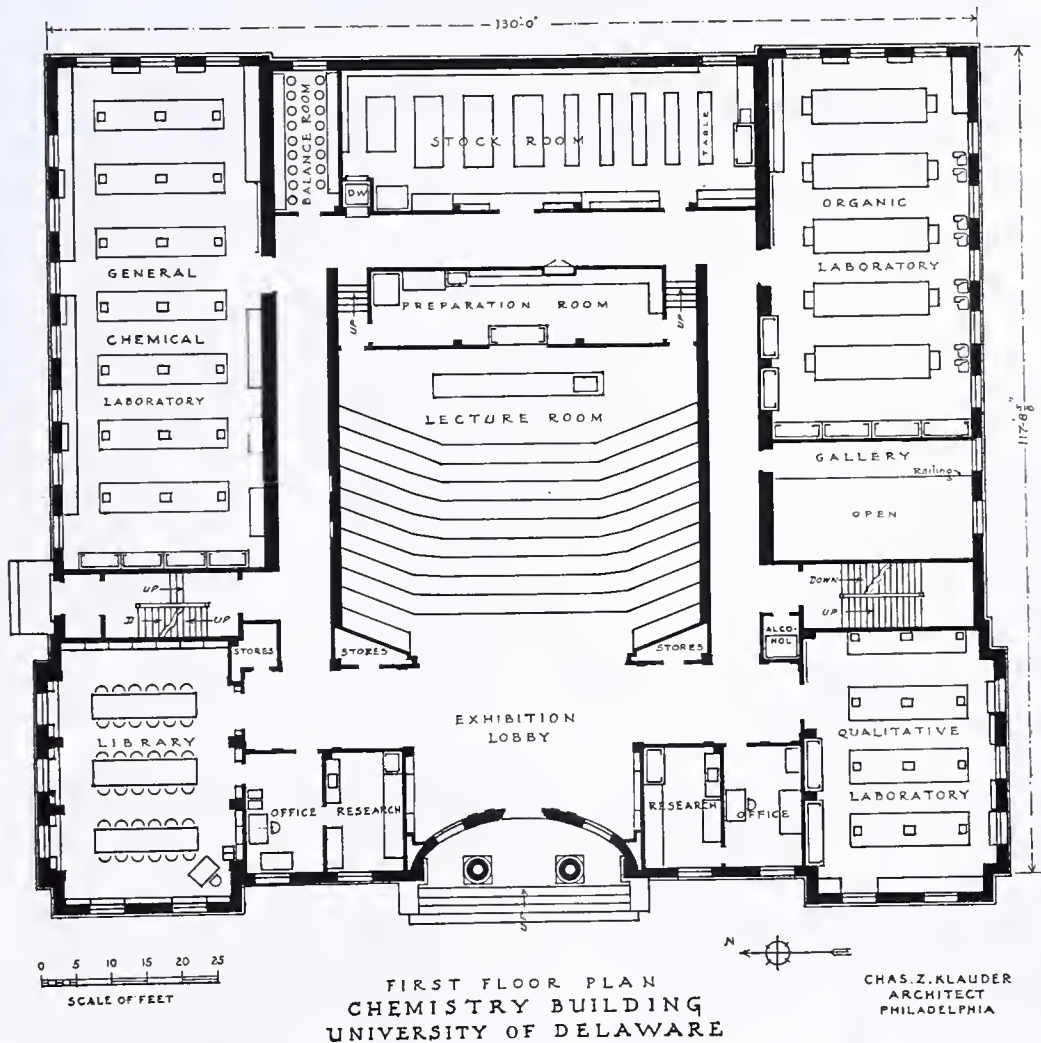
There is a down-draft hood on each desk in the general and qualitative laboratories, and all the laboratories, including the private rooms, are provided with hoods, some of the open-front type. The table and wall hoods are fitted with local dampers to control the volume of air removed. The room ducts are fitted with volume-control dampers in the attic at the junction with the main ducts.

Air removed from the main laboratories is supplied in part by the ventilating heater units from outdoors and in part through louvers in the doors to the corridors. This system gives a good draft of air from the corridors into the laboratories, and keeps the corridors free from fumes.

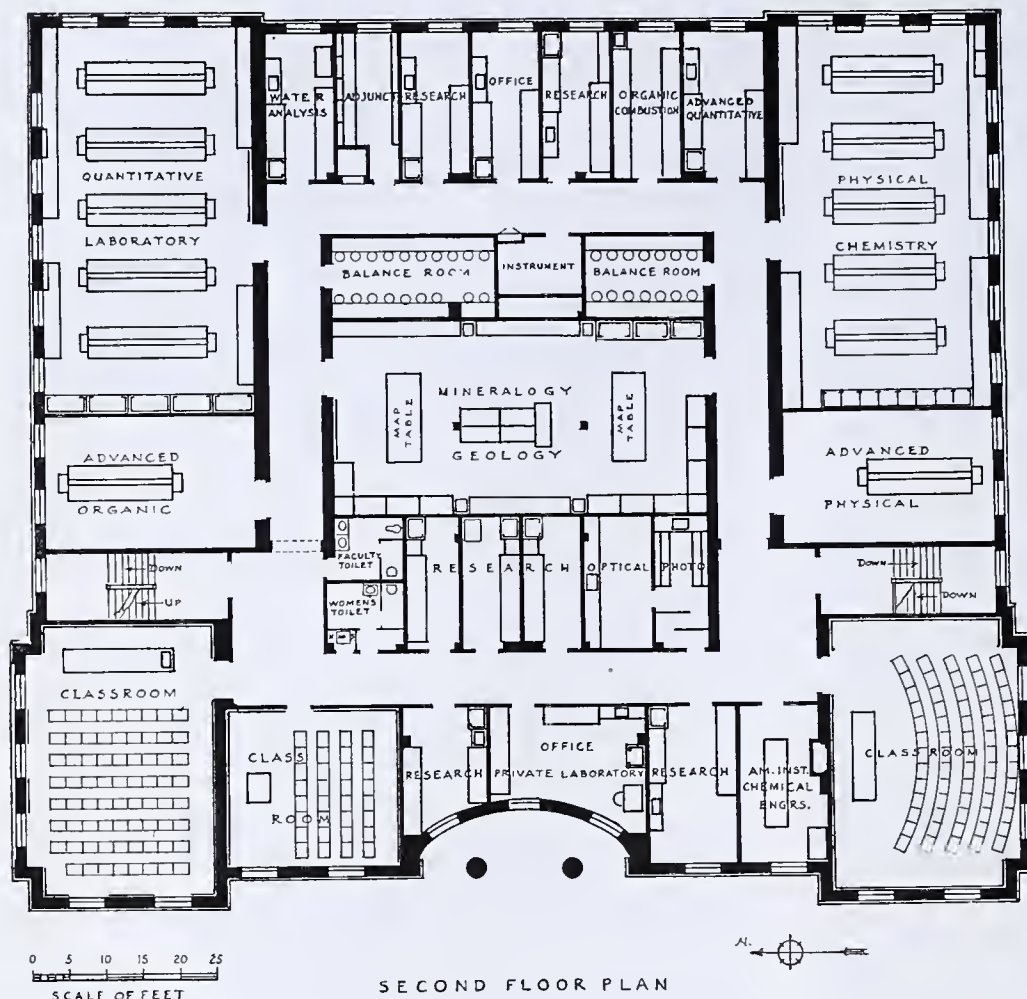
EXHAUST SYSTEMS. System I serves the main laboratories on the north side of the building with a fan removing 12,000 cubic feet per minute, driven by a 5-horsepower motor.

System II serves the main laboratories on the south side of the building with a fan having an air removal of 9400 cubic feet per minute, and a 5-horsepower motor.

System III serves several small laboratories and the lecture room, with an air removal of 7600 cubic feet per minute, using a 3-horsepower motor.







System IV serves the qualitative laboratory only, with special provision for hydrogen sulfide fumes, having an air removal of 4300 cubic feet per minute with a 2-horsepower motor.

System V serves a number of small rooms with an air removal of 4300 cubic feet per minute, using a 2-horsepower motor.

All these motors are connected to the fans with a V-belt drive, and work against a 1.5-inch resistance pressure.

The total air removal with all systems in operation is about 36,000 cubic feet per minute with a total of 16.5 horsepower for all motors.

The ducts leading from the hoods are 6 per cent antimonial sheet lead with all joints and seams burned. Approximately 30 tons of lead in weights of 3, 4, and 6 pounds per square foot were used. The ducts are partly rectangular and partly circular in form, and are reinforced with heavy band-iron overlaid with lead, all seams being burned. Rigid structural supporting members are essential to prevent sag or distortion of the lead.

All the principal laboratories, the lecture room, and the mineralogy room have special combination heating and ventilating units which deliver warmed out-of-doors air for both warmth and ventilation. These are connected to a dual system of pneumatic temperature control. The small rooms have steam radiators equipped with self-contained temperature-control valves.

All drainage from the sinks, including those in the hoods, is by a separate system made of acid-resisting high-silicon cast-iron pipe for all work above the basement, where connection is made to extra heavy terra cotta acid clay tile, extended to the campus drainage system. All the joints in the cast-iron lines are made with asbestos gaskets and

caulked lead. The tile pipe is made up with hot-poured bitumastic acid-resisting compound.

### Electrical Service

Electrical service for the building is taken from the campus underground distribution system, 2300-volt, 3-phase, 60-cycle. Transformers provide for 120- to 208-volt, 3-phase, 4-wire distribution for light feeders and 208-volt, 3-phase, 3-wire distribution for power requirements. The power and light panels are dead-front, "no-fuse," circuit-breaker type.

The general lighting is by means of ceiling lens-type lighting units in metal boxes, some of which are surface-mounted against the concrete ceilings and some set flush in the hung ceilings.

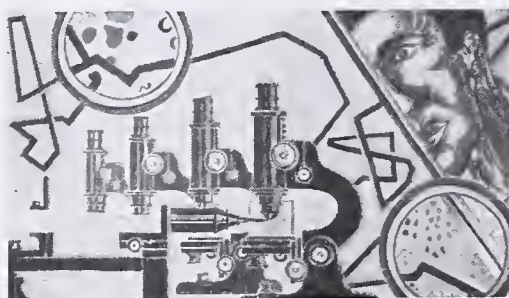
Direct current is distributed to all the laboratories by a separate system, which includes two 3-kw. motor-generator sets, a storage battery, and special distribution panels of plug-bus cordless type, capable of providing direct current in 2-volt steps from 2 to 24 volts and also at 110 volts.

### Lecture Room

The lecture room has 270 seats, and is without outside light or ventilation. It has a separate heater unit in the attic delivering about 4000 cubic feet per minute of outdoor air through streamline grilles, to maintain a uniform room temperature. The air exhaust is by gravity through outlets near the floor. In summer the unit may be operated at high speed for general ventilation. The air-intake duct and gravity roof ventilator are fitted with pneumatically controlled dampers which are open when the system is in use and closed at other times to prevent unnecessary loss of heat.

The lights in the lecture room are controlled by Thyatron dimmer equipment, which may be operated either at the lecture table or at the rear of the room. Special lights over the lecture table and another set of lights to illuminate the blackboard back of the table may be independently controlled. At the lecture table a push button on a flexible cord may be plugged in for the use of a speaker showing lantern slides, to operate a small signal light, which may be plugged in on a flexible cord by the lantern operator. There is also a sound movie installation for 16-mm. film, and a spotlight for special intense illumination of limited areas of the blackboard or lecture table.

The lecture-room floor is sloping and the preparation room is at the lower level. By raising the center section of the blackboard back of the lecture table, apparatus may be passed to and from the preparation room where lecture material is prepared and stored. This room is a fully equipped laboratory as well as store room.







# Microchemistry

## Paper as a Medium for Analytical Reactions

### A Method of Applying Reagent Papers to Large Volumes of Solution

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A DISTINCT advantage of the use of slightly soluble or "fixed" impregnants in reagent papers is the localization of the reaction in or near that area receiving the liquid under test. The reaction product thus concentrates on the fibers of a restricted area while the liquid, depleted of the ion precipitated, flows away. In the first article of this series (1), the application of this principle to "spot" tests was discussed. The solution is introduced from a capillary orifice, liquid flow being maintained by absorptive spreading in the surrounding paper. The volume handled in this manner cannot conveniently exceed 0.1 or 0.2 cc. For most purposes, especially where the test drop represents the final product of a series of separations and its dilution is not great, this quantity is sufficient.

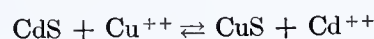
There remains, however, the case where the substance under test is present in very low concentration, and consequently a large volume of solution must be taken. Reduction of this volume may be impracticable because of the high concentration of other salts with which the substance sought may be associated, for example, as an impurity. It may be undesirable because of the loss of time involved, as in the examination of waters or soil extracts.

Under suitably chosen conditions, it is still possible to effect the removal of microgram quantities of an ion from large volumes of solution by means of reagent papers. In the method here reported the solution is caused to flow through a restricted area of the paper at a controlled rate. The paper is held across the liquid stream between two tightly compressed flanges. Reaction occurs essentially at the coated fiber surfaces and the product is retained by fixation thereon. When a color change results, direct comparison of the colored area with standards identically prepared may provide an approximation of quantity. If more precise determinations are required or the simultaneous removal of more than one ion by the paper necessitates subsequent separation, ashing or digestion of the spot then permits operations on a true micro scale.

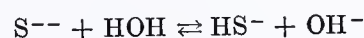
Three fundamental requirements must be met if a reaction is to be used in the proposed manner:

1. The impregnating reagent must be sufficiently insoluble to withstand the action of the large volume of solution flowing through a small area of the paper.
2. Sufficient difference must exist between the solubilities of reagent and reaction product to ensure reasonably quantitative precipitation of the ion sought.
3. The reaction product must be capable of immediate fixation on the fibers of the paper.

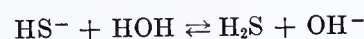
Consider, for example, the reaction between cadmium sulfide paper and copper ion:



Practical use of this reaction for the separation of traces of copper is discussed below. For present purposes, suppose a liter of the test solution is passed through a small area of paper, impregnated with cadmium sulfide, and that this percolation yields an outflowing solution which is saturated with cadmium sulfide. The dissolved cadmium sulfide dissociates to give equivalent concentrations of cadmium ion and sulfide ion, but the latter reacts with water to give largely hydrosulfide ion and un-ionized hydrogen sulfide:



and



where (at 18° C.)

$$\frac{[\text{S}^{--}] \times [\text{H}^+]}{[\text{HS}^-]} = 1 \times 10^{-16} \quad (1)$$

and

$$\frac{[\text{HS}^-] \times [\text{H}^+]}{[\text{H}_2\text{S}]} = 9 \times 10^{-8} \quad (2)$$

Equations 1 and 2 take into account the acidity of the solution. Assuming the hydrogen-ion concentration to be 0.01 molar, from 1,

$$[\text{HS}^-] = 10^{13} [\text{S}^{--}] \quad (3)$$

and, combining 2 and 3,

$$[\text{H}_2\text{S}] = 10^{18} [\text{S}^{--}] \quad (4)$$

Now, at 18° C.,

$$[\text{Cd}^{++}] \times [\text{S}^{--}] = K_{\text{CdS}} = 3.6 \times 10^{-29} \quad (5)$$

But,

$$[\text{Cd}^{++}] \approx [\text{CdS}] \quad (6)$$

the molar concentration of dissolved cadmium sulfide, and

$$[\text{CdS}] \approx [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{--}]$$

or

$$[\text{S}^{--}] \approx [\text{CdS}] - [\text{H}_2\text{S}] - [\text{HS}^-] \quad (7)$$



Combining Equations 3 and 4 with 7,

$$[S^{--}] \approx [CdS] - 10^{18} [S^{--}] - 10^{13} [S^{--}]$$

or

$$[S^{--}] \approx \frac{[CdS]}{10^{18}} \quad (8)$$

From 5, then,

$$[Cd^{++}] \times [S^{--}] \approx \frac{[CdS]^2}{10^{18}} \approx 3.6 \times 10^{29}$$

or

$$[CdS] \approx 6 \times 10^{-6} \quad (9)$$

Combining 8 and 9,

$$[S^{--}] = \frac{[CdS]}{10^{18}} = \frac{6 \times 10^{-6}}{10^{18}} = 6 \times 10^{-24} \text{ mole per liter}$$

in a saturated solution of cadmium sulfide.

In actual practice, however, the molar concentration of sulfide ion available is expressed by

$$q \times 6 \times 10^{-24} \text{ mole per liter}$$

where  $q$  is a fractional factor denoting the degree of saturation attained by the outflowing solution. This will depend on the conditions maintained in practice, chief among which are the rate of flow, the area of paper exposed, and the nature of the layer being precipitated over the cadmium sulfide-coated fibers.

Now assume the solution to contain a small amount of copper. As the copper ions enter the cadmium sulfide region copper sulfide is precipitated to satisfy the mass action law expressed in the solubility product:

$$[Cu^{++}] \times [S^{--}] = K_{CuS} = 8.5 \times 10^{-46} \quad (10)$$

But, since

$$[S^{--}] = q \times 6 \times 10^{-24}$$

$$[Cu^{++}] = \frac{1.4 \times 10^{-21}}{q} \quad (11)$$

where  $[Cu^{++}]$  is the molar concentration of copper ion remaining in solution.

Thus, if a solution containing traces of copper attains 1 per cent saturation ( $q = 0.01$ ) with cadmium sulfide, the copper remaining unprecipitated will be:

$$[Cu^{++}] = \frac{1.3 \times 10^{-22}}{0.01} = 1.3 \times 10^{-19} \text{ mole per liter}$$

or  $8.3 \times 10^{-12}$  microgram per liter. Even if the degree of saturation attained were only 0.001 per cent, the recovery of 1 mg. of copper from a liter of solution would be quantitative enough for practical purposes.

When the solution is passed through a second paper, however, it will contain an excess of cadmium ion, equivalent in quantity to the copper precipitated on the first paper. This will repress the solubility of the cadmium sulfide at the second paper and reduce the sulfide-ion concentration available.

In the present case, the difference between the solubilities of copper sulfide and cadmium sulfide is so great that even this will not materially decrease the efficiency of recovery. When circumstances are less favorable, however, as will be the case in many other reactions, it is important to emphasize the necessity of adjusting conditions for as complete removal as possible of the ion under test by the first paper.

In the preceding discussion, the factor  $q$  was introduced because of the realization that only an infinitely slow rate of flow would permit equilibrium conditions to be approached. In the example chosen, efficiency of recovery is clearly dependent on factors influencing attainment of equilibrium

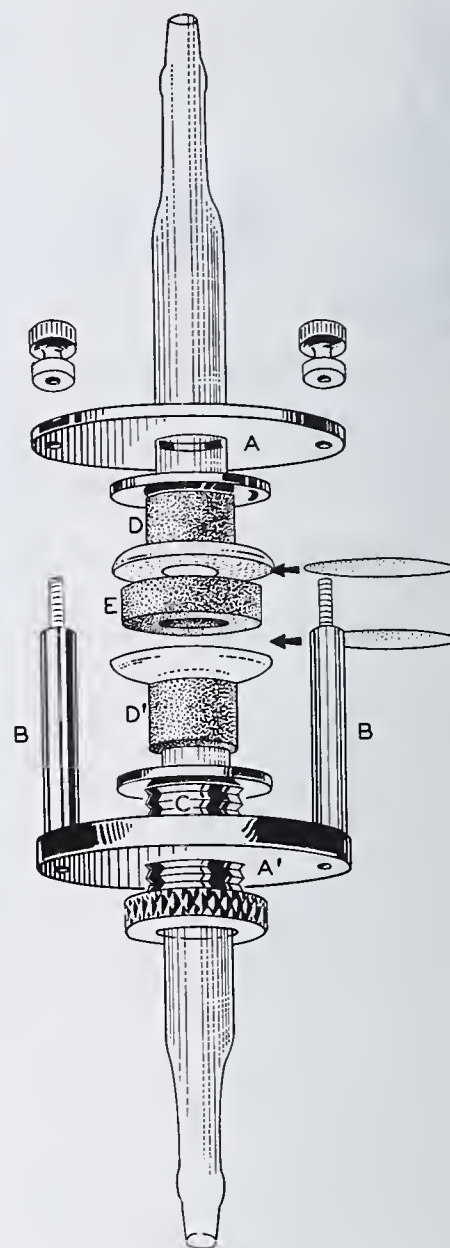


FIGURE 1. DETAILS OF FLANGE AND CLAMPING ASSEMBLY FOR HOLDING IMPREGNATED PAPER DISKS IN FLUID STREAM

rather than on the conditions of that equilibrium. Were saturation of the outflowing liquid with the impregnating reagent actually attained,  $q$  would, of course, become unity.

When relatively small differences between the solubilities of reagent and reaction product leave little working margin it becomes increasingly important to bring  $q$  as near to unity as possible. To accomplish this, flow should be reduced to the lowest practicable rate, while the exposed area of the paper should be as large as the estimable range of spot densities or as subsequent manipulations will allow.

The texture of the paper is also important. Very loose papers will have relatively large pores, through which the bulk of the solution will pass without opportunity for its ions to meet those of the precipitant or for the product to become fixed completely on the fibers. Tighter papers are required to afford sufficient reagent, to break up the capillary channels, to prolong the contact period, to ensure uniformity, and to provide sufficient mechanical strength. Of those tried, C. S. & S. No. 598 approaches the type which would seem desirable. Its thickness and wet strength are satisfactory. A somewhat closer texture and greater uniformity of pore size would improve its value in this work, however.



From the practical standpoint, it would seem that the method might still be applied advantageously to many types of impurity and "trace" analyses, even though recovery of the ion sought might reach only 90 or 95 per cent. Its simplicity guards against the manipulative losses which often make the more conventional approaches so uncertain that reproducible recovery of even such percentages cannot be counted on. Standardization of conditions for the reagent paper method results, at least, in a reproducible recovery, upon the basis of which estimations of quantity may be made. In a sample of nickel containing 0.005 per cent of copper, for example, it is seldom that the recovery of 0.0045 per cent would not be entirely acceptable.

### Apparatus

The apparatus used to confine the flow of large volumes of liquid through small definite areas of the impregnated papers is shown in Figures 1 and 2.

The unit consists of a pair of glass tubes, the ends of which terminate in heavy face-ground flanges, the plane of grinding being exactly normal to the axis of the tube. The flange openings have the same bore as that of the tube. (Such flanges may also be turned from Pontalite rod, thereby obtaining the advantages of accurate machining.) The paper is inserted between the flange faces, and pressure is applied by the clamp assembly shown. This consists of two brass plates, A and A' (Figure 1), separated by posts B. One of the flange tubes passes loosely through the hole in plate A; the other extends through the bore of the tightening sleeve, C, which is in turn threaded through a hole in plate A'. By tightening C, the flanges are forced together. Between the flange shoulders and the metal parts are heavy rubber compression cushions, D and D', which prevent breakage by providing the necessary elasticity. To prevent twisting of the flanges when the tightening sleeve, C, is turned, a graphite-lubricated washer is placed between it and the rubber cushion.

When it is necessary to pass the liquid through several paper disks in succession, a separation of these disks is usually desirable, especially when the first disk is unimpregnated and serves only to filter the solution. One or more hard-rubber separator rings may then be inserted between the flange faces. These rings have the same bore as that of the flanges and may be provided in various thicknesses to permit

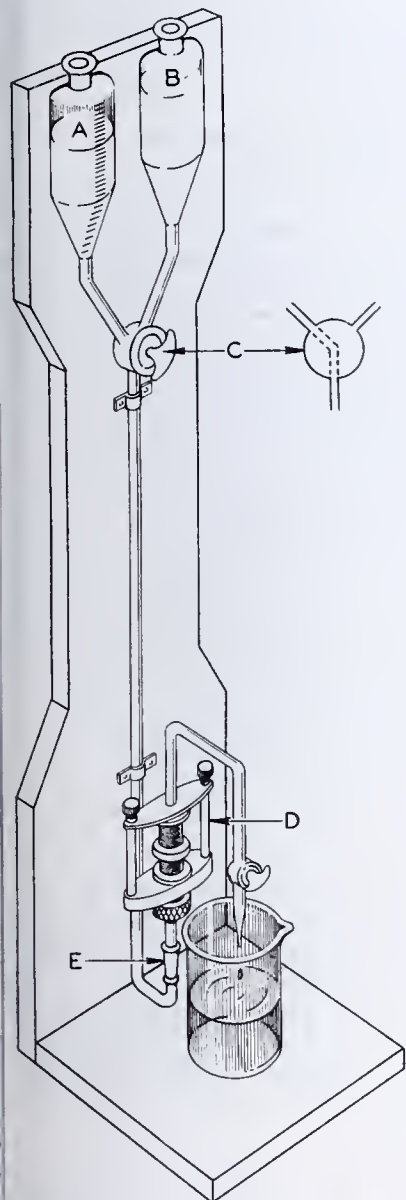


FIGURE 2. APPARATUS ASSEMBLY FOR RECOVERY OF TRACES FROM DILUTE SOLUTIONS ON IMPREGNATED DISKS

- A. Reservoir containing solution
- B. Reservoir containing wash liquid
- C. 3-way stopcock
- D. Flange-clamping assembly
- E. Standard ground-glass joint to facilitate removal of clamping assembly

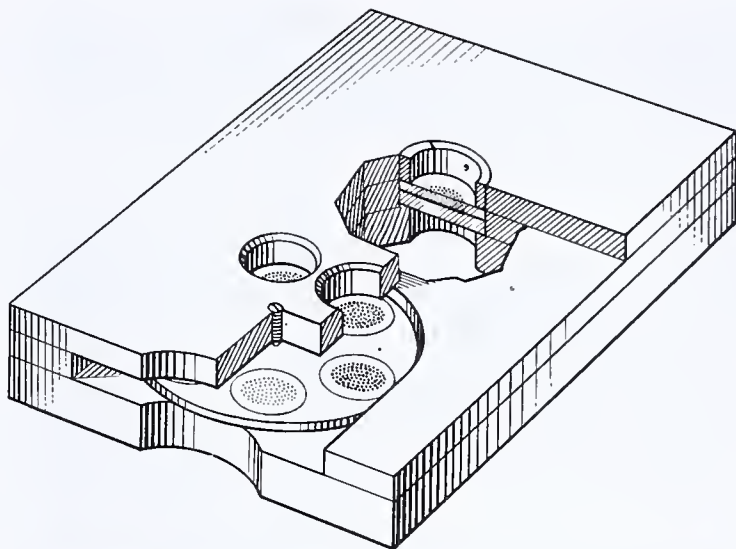


FIGURE 3. STANDARD SPOTS MOLDED IN LEUCITE WITH DETAILS OF COMPARISON BLOCK

variation of the distance between the papers. They provide a convenient alternative to the use of two or more separate flange and clamping assemblies. The rings are soaked in hot paraffin for several minutes to seal the surfaces coming in contact with the solution as a protection against adsorption or possible reaction with the ions being precipitated in the paper. When the conditions for a particular reaction are not already precisely established, or the quantities involved are not known, it is advisable to use several papers in series, since then completeness of removal in the first paper may be checked by examination of those that succeed it.

For approximation of quantity by comparison of spot densities, it is convenient to have prepared a series of standard spots made under conditions identical with those of the test. The permanent preservation of these standard spots often presents a problem because of deterioration brought about by the action of air, light, and moisture. Dipping in paraffin is commonly practiced, but this form of protection necessitates further mounting. For sulfide spots the authors have tried the experiment of molding the paper disks in Leucite. Three months after preparation the spots appear to be entirely stable; a more definite report on their stability will be given in a subsequent publication. The method is as follows:

In a shallow cylindrical mold (7.5 cm., 3 inches, in diameter) a layer of Leucite molding powder sufficient to give a finished disk 0.16 cm. (0.06 inch) thick is placed. Two such disks are formed at 175° C., and under 2700 to 4500 kg. (6000 to 10,000 pounds) pressure. The papers with the spots are then placed in a symmetrical arrangement on the face of one of the disks, after which the other disk is placed over it. The two disks with the spots between them are now returned to the mold and heated at 125° C. under 4500 kg. (10,000 pounds) pressure for 0.5 hour. On removing, a perfect sealing of the papers within a disk of the transparent material will have been accomplished. Such



disks are polished and mounted on a black Bakelite comparison panel as shown in Figure 3. By rotating the disk, the standard spots are brought, two at a time, under circular windows for comparison with the unknown spot placed under a similar window. The molding press used was one manufactured by the S. S. White Co., for dental work.

For greater precision in comparing the densities of spots produced on paper disks, either by liquids or gases, the authors are at the present time working on a colorimeter assembly in which the specimen spots may be compared directly with those obtained from standard solutions or gases in a paired flange assembly. By this procedure, a measured volume of the unknown fluid is allowed to pass through the flange at a definite rate until a spot of measurable density is obtained. The standard solution or gas is then run through the other flange until the same density of spot is obtained. By comparing the volumes, more reliable quantitative results are obtained than when the dried unknown spot is matched against a series of standards. A report is expected on this work in the near future.

### Preparation of Reagent Papers

Difficultly soluble compounds may be incorporated in the paper in two ways. When the water-insoluble reagent is soluble in a suitable organic solvent such as alcohol, acetone, benzene, or ether, the process is simple—that of dipping, blotting off the excess, and drying. Substances such as  $\alpha$ -benzoinoxime and  $\alpha$ -benzildioxime are examples. Fixed inorganic impregnants, for which such solvents do not exist, must be precipitated directly on the paper fibers. This is generally done by successive immersion in solutions of the substances which react to give the desired difficultly soluble product. In a few cases, however, a substance may be introduced into the paper in soluble form and by exposure to gas or vapor, by evaporation, or by the action of physical agencies such as light or heat, may be converted to the final "insoluble" product.

When successive dipping is the method, the density and uniformity of impregnation are controlled, respectively, by the quantity and distribution of one of the two reacting substances introduced by the first immersion. The excess liquid is removed by passing the paper through a small wringer with pressure between the rolls maintained at a definite value. To ensure complete uniformity, the paper must be fed into the wringer at a uniform rate. Between immersions, the paper is dried. If this is not done, the second solution will not be taken up by the paper, and precipitation of the reagent, instead of taking place at the fiber surfaces, will be superficial, yielding a nonadherent product which floats away from the paper surface.

The exact technic of immersion is important. The paper, cut to a size permitting easy manipulation, is lowered into the solution at a fairly rapid, uniform rate. If this practice is not followed and the operator's hand hesitates for an instant, the solution may rise by capillarity above the level of the liquid in the vessel. When this occurs, the concentration of solute in the advancing wet boundary is usually reduced through adsorption and does not adjust itself to that of the solution when fully immersed. Each time this happens, therefore, a streak on the finished paper results. In the second immersion, the effect is even more marked. Then, if the solution is allowed to rise in the paper, precipitation quickly depletes it of reactive ions, after which the advancing liquid dissolves and carries with it the salt with which the paper was impregnated in the first step. A narrow band, practically devoid of reagent, followed by one of abnormally heavy impregnation just above it, is the final result. Non-uniformity is also caused by changed absorptiveness of the paper along fold or wrinkle lines. Local moistening caused,

for example, by splashing or by wet fingers prevents entry of solution on immersion and leads to spottiness. On salt-impregnated papers it gives rise to capillary concentrations of the soluble salt and hence spoils completely the chances of obtaining a uniform product. Figure 4 shows such dipping striations on a typical paper.

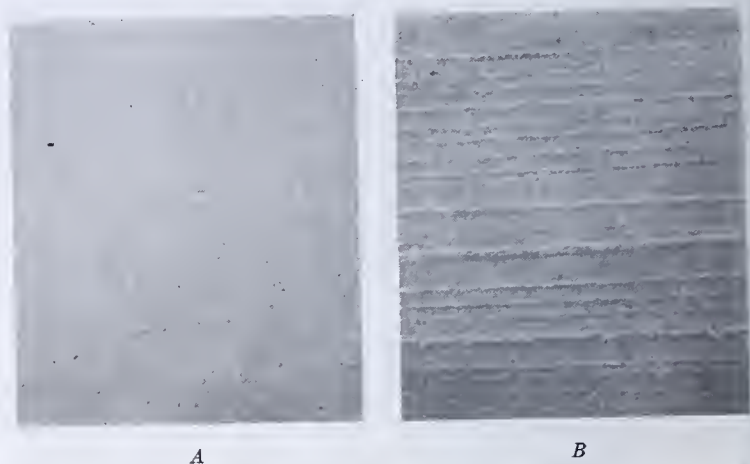


FIGURE 4. REAGENT PAPERS, PROPERLY AND IMPROPERLY PREPARED

Zinc ferrocyanide paper, developed in copper solution to render impregnation visible

- A. Uniform paper, properly impregnated
- B. Paper showing striations produced by slow, interrupted immersion during impregnating process

When the nature of the process permits, it is desirable to incorporate in the first treatment of the paper that ion an excess of which would be undesirable in the finished paper. If, because of the instability of the salt, this is not feasible, then final reimmersion of the paper in the first solution usually accomplishes the same end. For example, cadmium sulfide is used not only as an "insoluble" impregnant but also as a source of sulfide ion of controlled concentration. The presence of traces of sodium sulfide remaining in the paper would defeat the latter purpose and metals such as zinc or nickel might be precipitated. Sodium sulfide, because of its instability and caustic alkalinity, cannot, however, be used as the first impregnant because it cannot be dried satisfactorily on the paper. Therefore, the cadmium salt is introduced first and its sulfide precipitated with sodium sulfide. After washing, traces of the latter which may remain are removed by reimmersion of the paper in the original cadmium solution. A trace of free cadmium ion is not objectionable.

Washing of the paper is best done by spreading it on an inclined glass plate over which the flow of wash water is spread by a glass tube having a number of perforations. Unless the tap water is of exceptional purity, distilled water should be used for the initial washing, and in any event it should be used for the final wash. The amount of washing necessary will vary with the particular paper, of course. When the reagent is not extremely insoluble, care must be taken not to prolong it unduly. Sometimes in such cases it is better to leach out most of the salts in dilute alcohol or other media in which the impregnant is less soluble before applying a final short washing.

Overheating should be avoided in drying. A convenient oven can be constructed of a wooden cabinet using incandescent bulbs as the heating source. The papers should be protected from the strong light by a suitable baffle. The papers in general keep best when in tightly compressed packages away from light and laboratory fumes.

The density of impregnation may be computed approximately from the concentration of the solution in which the paper is first immersed and the liquid capacity of the paper used. The latter value is obtained by weighing a given area



of the dry paper, then weighing the same area after wetting with water and passing through the wringer. From the dry and wet weights and the area, the volume of liquid taken up by 1 sq. cm. of paper is determinable. The concentration of the solution used in the first immersion can then be adjusted to provide the desired density of precipitated reagent in the finished paper.

Papers to be used in the liquid stream should be impregnated as heavily with reagent as is consistent with uniform flow through the fibrous interstices. Such impregnation, therefore, should be accomplished by building up reagent layers on the fiber surfaces rather than by filling the interstices, for in the latter case interference with the flow would lead to channeling and to mottled spots. This desired type of precipitation results only when the paper is dried between immersions. When the impregnant is a colored compound such as cadmium or antimony sulfide, matching of spots, especially when faint, is usually enhanced by removal of the excess reagent. Subsequent treatment of the spot may also make presence of impregnant undesirable. In such cases appropriate treatments which leave the reaction product untouched but dissolve the impregnant may be devised. For example, antimony sulfide may be removed from copper, bismuth, or silver spots by treatment with dilute ammonia or alkali.

Technic

Disks of the impregnated paper, of diameter slightly smaller than that of the flange, are cut with a cork borer. In setting up the flange assembly, it is of course imperative that no air bubbles edge beneath the paper, since this would prevent exposure of a portion of it to the liquid stream, producing an uneven stain. For this reason, the best practice is to bring the solution in through the bottom of the vertically supported assembly. With the tightening screw released, water is allowed to flow from the washing reservoir (Figure 2) until the rubber connecting tube is free of air bubbles and a continuous column of liquid is obtained which overflows at the lower flange. The moistened paper is then laid over this flange, after which a further few drops of water are allowed to exude in order to expel any fine bubbles trapped beneath the paper. If the hard-rubber spacer is used, this is held against the lower flange with the fingers and water is again admitted until it fills to overflowing, when the second paper is put in place. The operation is repeated on the next spacer and so on. Finally, the upper flange is brought down on the paper and the clamping sleeve is tightened. The assembly is then ready for passage of the solution from its reservoir. Care should naturally be taken to ensure freedom from dust or fine precipitates which would be filtered out on the reagent paper and obscure the reaction product. In fact, it is always good practice to insert a filter paper disk, separated from the reagent papers by a spacer ring, to act as a cleaner.

Experimental

The writers have confined the present introductory studies largely to the precipitation of copper on cadmium sulfide paper, as a typical application. Reactions with metals such as copper, silver, mercury, bismuth, and lead, involving separation on papers impregnated with light-colored insoluble sulfides, are especially suited to this technic. Both reagent and reaction product have high degrees of insolubility, yet sufficient solubility differences often exist to ensure essential completion of the metathetical reaction. Further, the widespread necessity for determining minute amounts of such metals in great dilutions would seem to justify this starting point. In the writers' laboratory the examination of waters associated with corrosion problems, as well as the determination of impurities in nickel, aluminum, and other metallurgical products, has given first importance to these reactions.

COPPER REMOVAL ON CADMIUM SULFIDE PAPER. Sheets of S. & S. No. 598 paper are first immersed in a 15 per cent

solution of cadmium acetate, passed through the wringer, and dried in warm air. In this and the following operations, the precautions discussed in the general part of this paper are to be carefully observed. The dried cadmium acetate sheets are then immersed in 5 per cent sodium sulfide solution, washed thoroughly in pure running water, and dried. Finally the sheets are reimmersed in a 5 per cent cadmium acetate solution and again washed and dried. Three disks of the cadmium sulfide paper, separated by 0.6-cm. (0.25-inch) spacers, were clamped between flanges of 1-cm. diameter. Through such arrangements were passed varying quantities of water, 0.01 molar acid, and 0.1 molar sodium acetate solutions. The papers were then examined to determine the extent to which the cadmium sulfide was depleted in the areas exposed to the flow. The examination was aided, in doubtful cases, by conversion of the cadmium sulfide to brown-black copper sulfide by immersing the spot in copper sulfate solution. The results are shown in Table I.

TABLE I. STABILITY OF PAPERS (At 20° C.)

No.	Fluid	Vol- ume Cc.	Flow Rate Cc./min./ sq. cm.	Depletion of CdS Impregnant		
				1st disk	2nd disk	3rd disk
1	Water	1000	1	Slight	None	None
2	0.01 molar H <sub>2</sub> SO <sub>4</sub>	1000	20	Marked	Considerable	Slight
3		1000	1	Practically complete	Moderate	None
4	0.01 molar H <sub>2</sub> SO <sub>4</sub> +0.1 molar NaAc	500	1	Marked	Slight	None
5		100	1	Slight	None	None
6		1000	1	Appreciable	Very slight	None
7		500	1	Slight	None	None

These experiments show the effects of acidity and rate of flow on solution of the cadmium sulfide impregnant. As might well be reasoned, the slower the flow, the more nearly saturated is the outflowing liquid and the more cadmium sulfide is dissolved. With water, solution is so slight, even at the slow flow rate of 1 cc. per minute per sq. cm., that a liter removes only negligible quantities from the first paper, the others being unaffected. Hundredth-molar acid naturally dissolves much more. A liter at the slow rate almost entirely removes the cadmium sulfide from the first paper, while the second shows appreciable loss of color; the third is relatively unaffected. When the 0.01 molar acid is passed at the fast rate of 20 cc. per minute per sq. cm., solution of the cadmium sulfide is still appreciable, but occurs to a much smaller extent than at the slow rate. Moreover, of the cadmium sulfide dissolved, far less is removed from the first paper and a much greater proportion is removed from the second. Even the third paper is visibly affected. At slow rates of flow, saturation seems to be practically attained at the first paper and the others are unaffected until most of the impregnant in the first paper is removed. Rapid flow, on the other hand, prevents anything approaching equilibrium at the first paper, so that the impregnant is to some extent removed by the unsaturated solution from the succeeding papers. Rate of flow, therefore, is certainly an important factor.

Despite the fact that acid in 0.01 molar concentration greatly increases the solubility of the cadmium sulfide impregnant, there is still sufficient of this in the three-paper system to provide for quantitative removal of 50 micrograms or less of copper on 1-sq. cm. areas from a volume of 500 cc. at 1 cc. per minute per sq. cm. Precipitation will be substantially complete on the first paper until enough solution has passed to deplete the impregnant, after which the second paper will receive the copper. However, it is advantageous if the precipitation of practically all the copper or other metal sought can be made to take place on the first paper, especially when the quantity is to be estimated by comparison with standard spots. Since in practice a neutral, unbuffered solution for analysis is troublesome to obtain, control of acidity is logically effected through use of a suitable buffer. In



TABLE II. IMPORTANCE OF RATE OF FLOW

(50  $\gamma$  of copper in 0.01 molar  $\text{H}_2\text{SO}_4$ , buffered with 0.1 molar sodium acetate)


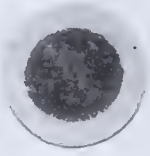
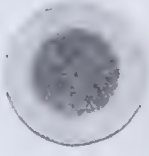



No.	Rate of Flow Cc./min./sq. cm.	Cadmium Sulfide Disk		
		First	Second	Third
1	20			
2	2			

TABLE III. RECOVERY OF COPPER

(20  $\gamma$  of copper, 0.01 molar  $\text{H}_2\text{SO}_4$ , buffered with 0.1 molar sodium acetate. Flow rate, 2 cc. per minute per sq. cm.)







Volume Cc.	Cadmium Sulfide Disk	
	First	Second
10		
100		
1000		

Table I it is evident that 0.01 molar sulfuric acid, when buffered with sodium acetate in 0.1 molar concentration, has little more effect on the cadmium sulfide impregnation than has water under the same conditions. In the succeeding experiments, therefore, the copper solutions were all buffered in this manner.

The rate of flow is important in other respects. If the solution passes through the paper at too rapid a rate, not enough cadmium sulfide is dissolved to provide the concentration of sulfide ion needed for complete precipitation of the copper. Further, insufficient time is allowed for reaction, growth of colloidal particles, and their fixation on the paper. An experiment which demonstrates this is summarized in Table II.

In this experiment the same volume of solution containing the same quantity of copper was passed through the papers at the two widely differing rates of flow. At 20 cc. per minute per sq. cm., recovery of the copper is not complete with three papers. At 2 cc. per minute per sq. cm., practically all is precipitated on the first paper.

Besides the above controllable factors, one which may impair the completeness of removal of the copper on the first paper is excessive channeling. This may be caused by exceptionally large pores resulting from faulty manufacture or by nonuniform impregnation. Very heavy impregnation


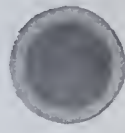


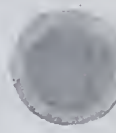
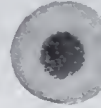
may close the finer interstices altogether, diverting the fluid stream at high velocity through the few large ones still open. The impregnated fibers lining such pores quickly become saturated with copper sulfide and depleted of cadmium sulfide and further removal of copper on that paper is no longer possible. A mottled spot results.

Figure 5 shows papers of this sort which were clamped together without a separator. The second paper receives high concentrations of copper where the solution streams through large pores of the first and the distribution of such pores is thus graphically reproduced. This experiment also emphasizes the desirability of using separators between papers to allow for redistribution of copper in the solution before it meets the next paper. Then, if there are minor nonuniformities or if such should develop, they will not affect the uniformity of the succeeding paper. Of course, if it is merely desired to recover the copper or other metal and not to estimate the spot density colorimetrically, uniformity is not so important and the separators may be dispensed with.

Under the conditions already discussed, recovery of copper is satisfactory in volumes ranging from 10 to 1000 cc. Table III shows 20 micrograms of copper recovered from volumes of 10, 100, and 1000 cc. The intensities of the resulting spots are identical within the limits of photographic reproduction.

TABLE IV. RELATION OF CONCENTRATION OF COPPER TO DENSITY OF SPOT

(Volume, 250 cc. Rate of flow, 2 cc. per minute per sq. cm. 0.01 molar  $\text{H}_2\text{SO}_4$ , buffered with 0.1 molar sodium acetate)

No.	Copper $\gamma$	Diameter of Flange Cm.	Area Ratio	Spot
1	22.5	1.5	9	
2	10	1.0	4	
3	2.5	0.5	1	
4	5	1.5	9	
5	5	1.0	4	
6	5	0.5	1	



That a given quantity of copper per unit area of exposed paper produces a spot of given density is shown in Table IV. The flanges used were 5, 10, and 15 mm., respectively, in diameter and the areas of the papers were consequently in the ratio 1 to 4 to 9, the ratio which was used for the concentrations of the three copper solutions—10, 40, and 90 micrograms in 250 cc. in tests 1, 2, and 3. These spots show the same densities. In tests 4, 5, and 6 the copper concentration was held constant, thus producing spots whose densities are inversely proportional to the areas.

Control of the flange size thus provides a device by which the sensitivity of the test may be regulated within practicable limits. A half microgram of copper is easily visible on a 1-sq. cm. area. By reduction of this area to 0.1 sq. cm., 0.05 microgram would be equally easy to detect. Further, estimation of quantity need not necessarily be made by comparison of spots of the same area, so long as the areas are known.

In Table V is reproduced a series of spots showing the recovery of varying quantities of copper between 1 and 100 micrograms from 500 cc. of solution on exposed areas 1 cm. in diameter. In these and other experiments cited in this part of the article, the excess cadmium sulfide was removed from the disk containing the copper spot immediately after

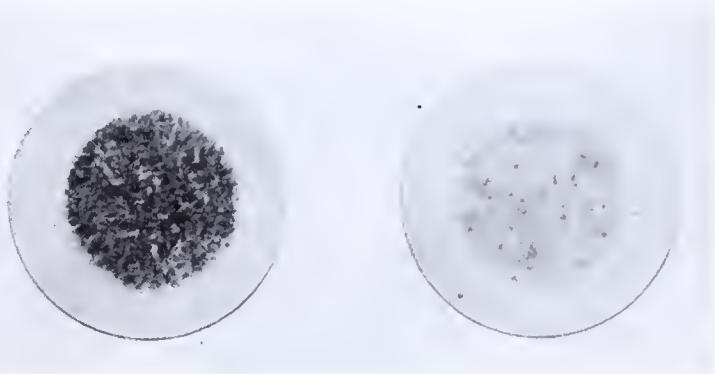


FIGURE 5. MOTTLED SPOTS (×2)


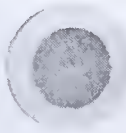


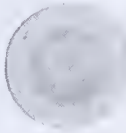
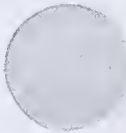
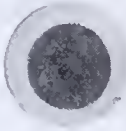

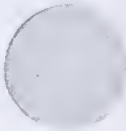
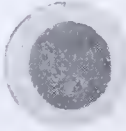

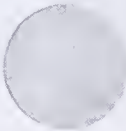
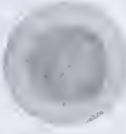
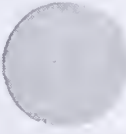
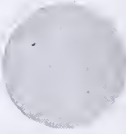
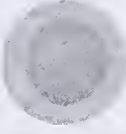

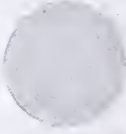
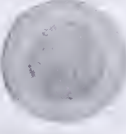

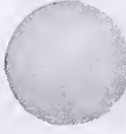
Showing effects of too heavy impregnation combined with absence of separator between successive disks.  
Liquid flow is thus restricted to the larger pores of the first paper because smaller ones are clogged. The second disk was too close to the first to allow a redistribution of the solute leaving it; hence it has reproduced the pore pattern of the first.

the solution had percolated through it. Removal is effected by repeated immersion in warm 1 molar hydrochloric acid, the excess acid being blotted off between immersions. The disk is then thoroughly washed in distilled water. If the spot is allowed to remain wet for long periods with the cadmium sulfide unremoved, a tendency towards conversion of the green-black copper sulfide to a brown-colored product has been noticed. Removal of excess impregnant with molar acid then fails to restore the original color of the spot and on treatment with 10 per cent potassium cyanide, which dissolves the copper sulfide, yellow spots of cadmium sulfide remain in the area which it occupied. Some of the cadmium sulfide apparently is rendered insoluble through prolonged association with the copper sulfide, possibly through formation of a double compound.

From Table V the following conclusions seem admissible:

1. Recovery on three disks is practically complete for quantities up to 50 micrograms. The 100-microgram series shows a spot density on the third paper corresponding approximately to 1 microgram. Hence we may assume that the quantity which passed unprecipitated was less than 1 microgram or 1 per cent of the whole. It seems, however, somewhat risky to trust recovery of this quantity to three papers using this area.
2. The quantity detectable is less than 1 microgram in 500 cc. Actually a spot on a 1-cm. flange opening was obtained with 0.5 microgram but because of uncertainty of photographic reproducibility this was not included. This corresponds, therefore, to one part per billion.
3. The range over which estimations may be made safely by comparison of spot densities is not altogether evident from the photographs shown. When the copper sulfide is deposited only in the fiber layers near the surface, into which incident light penetrates, density comparisons may be satisfactorily made with surface illumination—that by which the photographs were taken. Thus, up to 10 micrograms the gradation is readily seen. When the penetrable surface layers have reached their saturation point, however, further increase in spot density is observable only by transmitted light and hence the heavier spots do not show a significant difference here, although against an illuminated background of suitable intensity the gradation is still observable up to 50 micrograms.

Such a background is conveniently provided by the illuminator shown in Figure 6. This consists of a glass-topped box containing a tubular incandescent bulb, a diffusion screen above which is a slot for

TABLE V. COPPER REMOVAL ON CADMIUM SULFIDE PAPER						
(500 cc. of 0.01 molar H <sub>2</sub> SO <sub>4</sub> , buffered with 50 cc. of molar sodium acetate passed at 1 cc. per minute per sq. cm.)						
No.	Copper		Cadmium Sulfide Disk			
	Added	Concentration	First	Second	Third	
	γ	P. p. m.				
1	100	0.20				
2	50	0.10				
3	25	0.05				
4	10	0.02				
5	5	0.01				
6	2	0.004				
7	1	0.002				



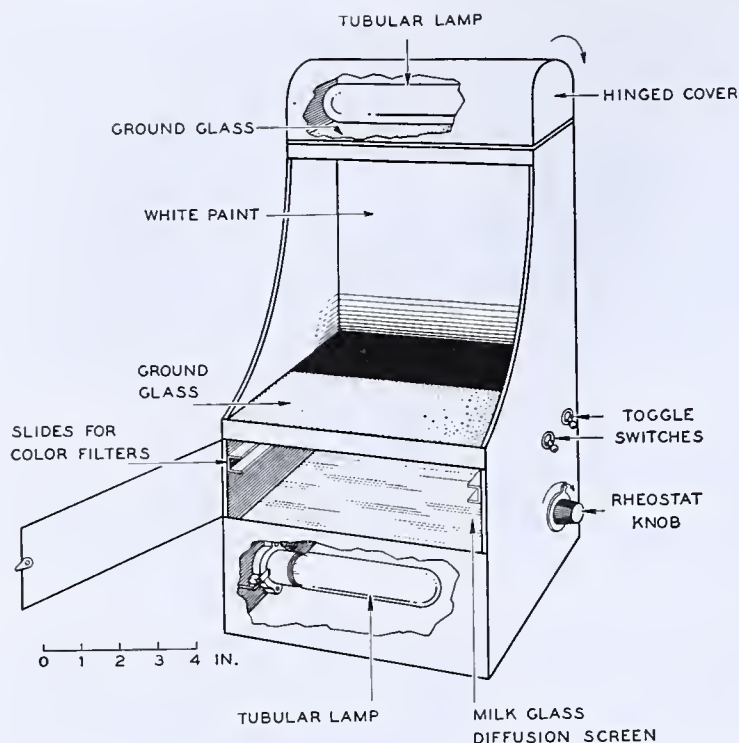


FIGURE 6. ILLUMINATING STAND FOR COMPARISON OF SPOTS

The stand is equipped to supply either incident or transmitted light. The latter is controllable by means of a rheostat and color filters.

insertion of color filter plates, and a rheostat for controlling the light intensity. A reproducible source of incident light is also included. The details are evident in the sketch. For the copper sulfide spots, a light yellow filter has been found to facilitate matching. In general, the range over which the matching is most accurate is from 0.5 to 10 micrograms per sq. cm.

TABLE VI. RECOVERY<sup>a</sup> OF COPPER ON CADMIUM SULFIDE PAPER

No.	Cu Taken γ	Cu Recovered <sup>b</sup> γ
1	20	19
2	20	19
3	20	21
4	20	20
5	50	48
6	50	49

<sup>a</sup> Conditions of Recovery:

Volume 500 cc.  
Solution 0.01 molar  $H_2SO_4$  + 0.1 molar NaAc  
Rate of flow 1 cc. per minute per sq. cm.  
Area of spot 0.8 sq. cm.  
Number of papers, each separation 3

<sup>b</sup> Readings on standard solutions were reproducible to  $\pm 1\gamma$ .

The sensitivity of cadmium sulfide paper for silver was found to be considerably greater than for copper. In a liter 0.2 microgram is still easily detectable on a 1-sq. cm. spot. The sensitivity for this area thus reaches one part in five billion.

The final proof of the completeness of recovery rests on the determination, by an independent method, of known quantities added to solutions and thus separated. To this end, spots from 500-cc. solutions containing 20 and 50 micrograms of copper were digested with nitric-sulfuric acid mixture, the excess was removed by evaporation, and the residue was dissolved in 2 per cent ammonium citrate. The solution was transferred to a small separatory funnel and to it were added 5 cc. of 1 per cent sodium diethyldithiocarbamate and 5 cc. of 1 to 1 ammonia. The brown copper diethyldithiocarbamate was then extracted with three portions of 5, 3, and 2 cc., respectively, of amyl alcohol. The extracts were

compared with standards in the Leitz universal colorimeter. The results are shown in Table VI.

## Applications

The primary purpose of this article is to present a general technic for the separation of traces, adaptation of which may be made to specific analytical problems. Nevertheless it seems desirable to conclude with a few briefly stated examples, illustrative of such adaptation.

**SEPARATION OF COPPER FROM NICKEL.** Buffered solutions of "pure" nickel containing up to 10 grams per liter of the metal can be passed through cadmium sulfide paper without affecting it, and from such solutions traces of copper are recoverable with the same ease as from a water solution containing the same quantity of copper alone. A few micrograms of copper in samples of nickel ranging in weight from a fraction of a gram to several grams may be separated and estimated, either from the density of the copper sulfide spot obtained or by colorimetric or titrimetric methods applied to the ashed paper. A convenient and rapid method is thus provided for the estimation of copper in commercial nickel or in nickel electroplating baths. The copper content may be estimated when as low as 0.0001 per cent.

**PROCEDURE.** Based on the copper expected, dissolve in 1 to 1 nitric acid a quantity of sample sufficient to provide 10 to 30 micrograms of copper. Evaporate off the excess acid, add perchloric acid, and fume to a moist residue. Dilute, adding 100 cc. of 0.1 molar sodium acetate for each gram of nickel present. Test the reaction with Congo Red paper. If still acid, add sodium acetate in concentrated solution, until the reaction is alkaline. Pass this solution, at 1 cc. per minute per sq. cm., through three cadmium sulfide disks in a 1-cm. flange assembly. When the nickel solution reaches the bore of stopcock C (Figure 2), turn this to admit a wash solution of 0.1 molar sodium acetate, continuing the flow until the liquid drains colorless. Remove the disks and transfer each to a micro-Büchner funnel for treatment to remove the excess cadmium sulfide.

A convenient assembly containing a number of these funnels with separate receivers is shown in Figure 7. (Such an arrangement is particularly useful where several successive treatments of the paper are necessary.) First place a disk of blotting paper on the perforated funnel bottom in order better to distribute the suction. Wash with warm 1.5 molar hydrochloric acid saturated with hydrogen sulfide until the yellow color of the cadmium sulfide is completely removed. Then wash with water until the paper no longer reacts acid. Remove and dry. If the quantity of sample was properly chosen, practically all the copper will have separated on the first disk and it may be estimated by comparison with standard spots.

TABLE VII. COPPER DETERMINATION IN "PURE" NICKEL

	Weight of Sample Grams	Time Required Total running time		Copper Found %
		Man-hours	Hours	
Macromethod <sup>a</sup>	10	3	10	0.0075 $\pm$ 0.0005
Micromethod	0.1	0.5	1.5	0.008 $\pm$ 0.002
Spot density	0.1	1	1.75	0.0085 $\pm$ 0.0005
Iodometric				

<sup>a</sup> Separation as sulfide with  $H_2S$ ; iodometric titration.

More precise determination can be made on the ashed spot. To avoid appreciable loss of copper, ashing requires careful control of the heating. Since this is not easily accomplished with a gas flame, the authors use the electrically heated crucible furnace shown in Figure 8.

Tall-form 2-cc. porcelain crucibles are used when ashing is combined with acid treatment. The winding, of platinum-rhodium alloy, conforms in shape to the crucible and is heated by a current supplied at 6 to 8 volts from a step-down transformer. Since it is only superficially imbedded in the Alundum furnace wall, the temperature lag is greatly reduced, making



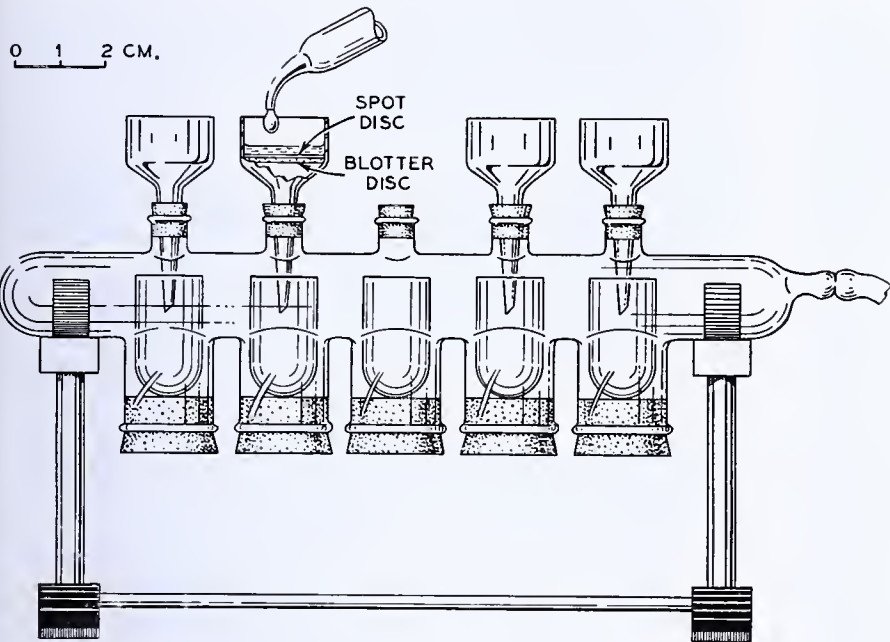


FIGURE 7. ASSEMBLY FOR TREATING SPOTS WITH LIQUID REAGENTS

possible an almost instantaneous heat control by means of a suitable rheostat.

The excess paper is trimmed away from the spot, which is then folded to a small pellet without touching the front surface and placed in the crucible, and the volatile matter is carefully distilled off without ignition. The crucible is cooled and a small drop of concentrated sulfuric acid is run down the wall to wet the carbonaceous mass. The acid is cautiously evaporated, after which the temperature is raised until a red glow in the residue indicates ignition of the carbon. The furnace heat is then cut off. When the residue no longer glows, another drop of acid is added, it is evaporated, and the temperature is raised to a barely perceptible redness ( $550^{\circ}$  to  $600^{\circ}$  C.) to complete burning of the carbon. Under no circumstances should the temperature be allowed to reach the decomposition point of copper sulfate ( $650^{\circ}$  C.).

To the residue in the crucible is added 0.05 cc. of glacial acetic acid, followed by warming for 1 to 2 minutes on a steam bath. A half cubic centimeter of water is then added, together with a small fragment of potassium iodide and a drop of starch solution. The liberated iodine is titrated with 0.001 N thiosulfate, added from a microburet graduated in 0.001-cc. divisions. A suitable stirrer may be made from platinum wire by fusing a bead at one end and beating this flat.

With proper equipment available, the whole procedure of ashing and titrating can be carried out in less than 15 minutes.

In devising other methods for estimation of the copper it should be remembered that the spot is contaminated with traces of cadmium sulfide which have escaped removal by the hydrochloric acid treatment.

Table VII presents data illustrating the time-saving feature of the proposed method. The precisions indicated, as well as the times, are to be taken only as approximations, since only one determination was made by each method.

**COPPER IN LEAD.** By a method similar to that just described for nickel, copper may be separated, along with most of the bismuth, from lead, thus facilitating its rapid estimation. From 0.1 to 1 gram of the sample is dissolved in nitric acid, and the solution is buffered and percolated through cadmium sulfide disks.

Lead separates with the copper, but this does not reduce the completeness of removal and the lead may be later dissolved out of the spot, together with the excess cadmium sulfide, by treatment with warm 1.5 molar hydrochloric acid.

The separation of silver from lead by this method is being studied by the authors.

**ESTIMATION OF TRACES OF LEAD IN WATER AND AIR.** From neutral solutions containing not too high a concentration of salts, lead may be removed on zinc sulfide paper with a sensitivity approximating that of the copper removal. Zinc and lead sulfides approach each other in solubility much more closely, however, and the reaction is therefore more susceptible to interferences than are those with copper, bismuth, or silver. Acetates in particular must be absent. The solution cannot contain high concentrations of such salts as nitrates and chlorides. Further, fixation of lead sulfide from solutions whose pH is above 8 is poor, the product being easily washed out of the disk because of its colloidal condition.

For the estimation of lead in drinking water, however, the method may have possibilities, particularly for field use, since nothing but the flange assembly and paper is required, estimation being made by spot-density comparison with standards. Copper sulfide may be removed from the spot

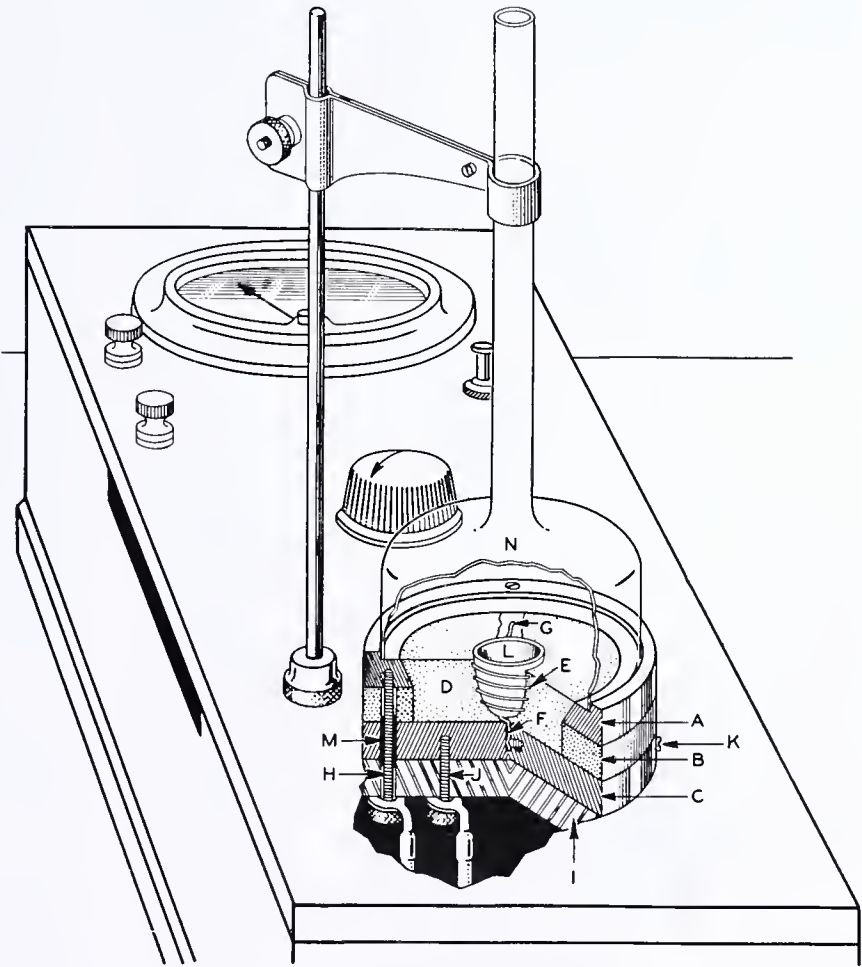


FIGURE 8. CRUCIBLE FURNACE MICROASSEMBLY

Ring A and plate C, of Duralumin, and separating ring B, of Transite, comprise the furnace body, mounted on Transite panel I. A and C are insulated from each other by B and glass bushings M and carry current to winding E, which is fastened at F and G. Current to the furnace is supplied through mounting screws H, to the top ring, and J, to the bottom plate. Space D is filled with Alundum cement, in which is molded the depression for crucible L. A glass bell protects the contents of the crucible from dust and drafts.



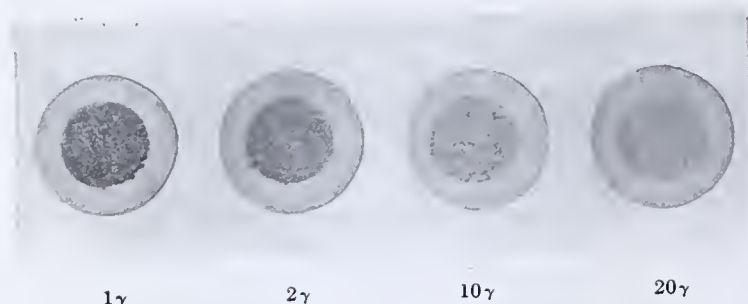


FIGURE 9. LEAD SPOTS ON ZINC SULFIDE PAPER  
Lead removed from 250 cc. of water

without affecting the lead sulfide by treatment with 5 per cent potassium cyanide.

Likewise the estimation of lead in air might be effected by the use of a suitable water impinger containing 1 to 2 per cent of nitric acid. At the completion of the air sampling, the solution is neutralized with potassium hydroxide, using methyl orange, and passed through the zinc sulfide paper.

Figure 9 shows spots obtained with neutral lead solutions through zinc sulfide paper.

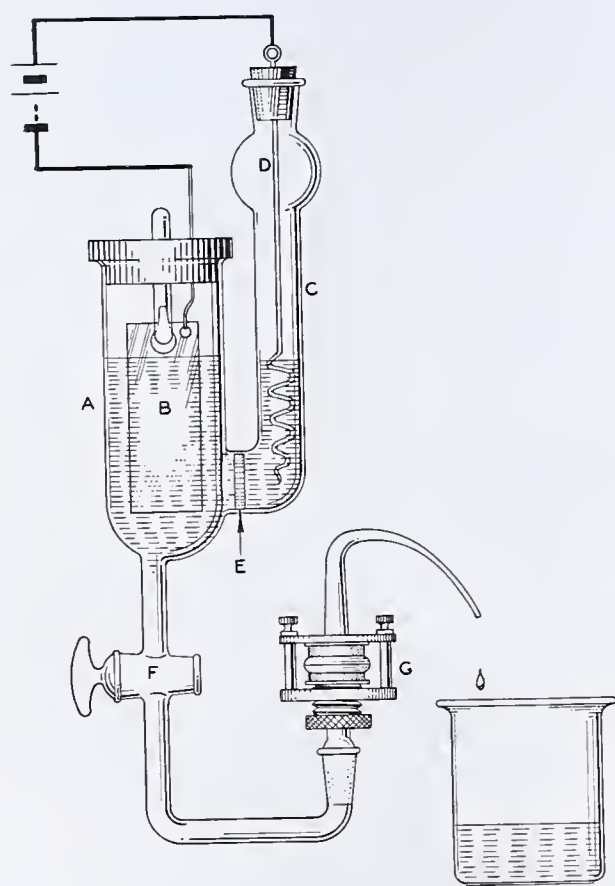


FIGURE 10. APPARATUS FOR CATHODIC REDUCTION OF TARNISH FILMS

- A. Cathode chamber
- B. Specimen (cathode)
- C. Anode chamber
- D. Anode (platinum spiral)
- E. Porous separator
- F. Stopcock for controlling rate of flow
- G. Flange assembly containing lead carbonate disks

**DETECTION AND ESTIMATION OF SULFIDE IN TARNISH FILMS.** Lead carbonate or phosphate paper can be used to remove sulfide ion, provided the solubility of the impregnant is reduced by an excess of phosphate ion and the pH is held between 7 and 8. This has furnished the basis of a convenient method for the detection of sulfide in thin tarnish films on

silver, copper, and other metals. The specimen is immersed in 2 to 3 per cent disodium phosphate solution and made the cathode of an electrolytic cell and any insoluble sulfide which may be present in the film is converted to sulfide ion by the reducing action at the cathode surface. The electrolyte is slowly drained from the cell with the current still on, passing directly through a flange assembly containing the lead paper. A few micrograms of sulfide on several square centimeters of metal thus are easily detectable. Quantitative estimation is possible by comparison of spot densities with standards. Figure 10 shows the details of the cathodic reduction assembly.

### Literature Cited

- (1) Clarke, B. L., and Hermance, H. W., *IND. ENG. CHEM., Anal. Ed.*, 9, 292 (1937).

RECEIVED December 21, 1937. Second in a series on "Paper as a Medium for Analytical Reactions," the first of which is indicated in reference (1).

## Determination of Iodine In Drinking Water, Urine, and Substances Containing Only About 1000 Times as Much Organic Matter as Iodine

A. C. BRATTON AND J. F. MCCLENDON, WITH THE TECHNICAL ASSISTANCE OF WILLIAM FOSTER AND RALPH WHITE

University of Minnesota Medical School, Minneapolis, Minn.

THE senior author has been engaged in iodine micro-analysis since 1922 (7) and was the first to make closed combustions on biological materials, both in a bomb (6) and a combustion tube (silica, 5). His method was improved by McCleendon and Remington (9) and McCleendon and Bratton (8).

Open ashing involves losses. Wet combustion has been used, but usually the reagents are about one hundred million times the weight of the iodine to be analyzed. In the work reported in the present paper the quantities of reagents have been reduced to a minimum—in fact, the only reagents added in more than milligram quantities are sulfuric acid, of which about 2 cc. are used (diluted to 3 cc. with water), and sodium hydroxide, of which less than a gram is usually all that is necessary.

The material is fused with sodium hydroxide in a nickel crucible, dissolved in water with a few milligrams of sodium azide, and transferred to a microstill (8, Figure 4). After boiling off most of the water in the still, and adding the acid, a little ferric iron, and 2 cc. of bromine water, the material is placed in a receiver. The iodine is now driven over with the rest of the water by flaming the trap as far as the cold part of the condenser. It is necessary to distill some of this sulfuric acid in order to recover all the iodine, because of the presence of traces of reducing substances (destroyed by 4 minutes' boiling of the sulfuric acid). The bromine in the receiver oxidizes the iodine to iodate. The excess iodate is removed by boiling and aeration. Potassium



iodide is added and the resulting iodine is titrated electrometrically with sodium thiosulfate.

## Procedure

This method is not applicable to ordinary tissues of land or fresh-water organisms but is applicable to samples containing only milligram quantities of organic matter, chlorides, and silicates, and at least 0.2 microgram ( $\gamma$ ) of iodine. It is, therefore, applicable to nearly all organic compounds containing iodine, as well as to thyroid gland, seaweed, sponge, gorgonians, and other tissues which contain relatively high percentages of organic compounds with iodine in their constitution. Although moderate amounts of chlorides or even bromides do not interfere, hydrochloric and hydrobromic acids pass over with the iodine during distillation; therefore an amount of chloride which when converted to acid would alone produce too great an acidity for the analysis is not allowed, and in fact, the sample should not contain more than half a millimole of chloride. The method is not applicable to sea water, brine, or even some mineral waters, but since the chlorides of drinking water are usually low, it is possible to analyze the iodine in less than 1 liter of drinking water.

The method is not applicable to soil samples because of their high silicate content, but soil solution may be analyzed (as drinking water), provided the chloride content is not over 0.5 millimole. Where larger quantities of alkali are used in fusion of the sample, or where water contains considerable alkali, more sulfuric acid must be used in the still.

Thyroid gland or marine animal or plant tissues are fused with alkali and a trace of rare earth oxide (as an oxidation catalyst) and transferred to the still with a few cubic centimeters of azide solution and double-distilled water.

Five cubic centimeters of urine containing 0.2 $\gamma$  of iodine may be analyzed, after destruction of the urea by fusing with 1 gram of sodium hydroxide and 2 mg. of mixed rare earth oxide (as an oxidation catalyst) until the last bubbles of ammonia are distilled off.

Whereas natural water samples are made alkaline by adding sodium hydroxide and azide (as a rule, 10 to 20 mg. of azide per liter are sufficient to destroy nitrite that would cause loss of iodine during evaporation), and then evaporated to dryness and fused with a trace of rare earth oxide before introduction into the still, chlorinated water is evaporated and fused before adding the azide, which not only destroys nitrite but reduces iodate.

**DISTILLATION.** The still used (8, Figure 4) is made of a 100-cc. round-bottomed, long-necked Pyrex flask with side neck close to the top. An inverted funnel is inserted in the neck as a trap to prevent the introduction of iron into the distillate in the form of spray (which would cause the results to be high). A hole is blown in the stem of the funnel and the tip is closed and sealed to the mouth of the flask, which is closed by fusion. A condenser is sealed to the side neck.

Any silica gel left in the still from the last distillation is dissolved out with sodium hydroxide. The air inlet of the still is connected with the compressed air supply, which introduces about one bubble a second. The condenser is connected with running water and the solution is evaporated in the still to about 3 cc. in volume. A 10-cc. test tube containing about 2 cc. of bromine water is placed as a receiver, 3 cc. of 21 *N* sulfuric acid are introduced through the air inlet, followed by 0.2 cc. of 4 per cent ferric sulfate solution, and the air stream is continued. As the solution is evaporated, if chlorides are present in the sample, hydrochloric acid will distill over.

When fumes of sulfur trioxide appear in the still, the gas flame of the microburner is reduced to 5 mm. and distillation is continued for 2 minutes. After about 1 minute of this period the trap in the neck of the distilling flask is heated with a large flame until all the moisture has disappeared. Since the water seal of the trap is evaporated and therefore the trap is not now functioning in the normal manner, the still must be carefully watched for 4 minutes; no spray should be allowed to pass into the condensing tube, as any iron in the distillate will destroy the accuracy

of the results. At the end of the 4 minutes of fuming, the condenser outlet is washed with a little water and the receiving tube is removed.

**EVAPORATION OF EXCESS BROMINE.** The receiving tube is placed in a boiling water bath and air is bubbled through a capillary lowered into it until the bromine is evaporated (color disappears) and for 10 minutes longer, then cooled in melting ice.

**TITRATION.** A 1-cc. buret (4) graduated in thousandths is used. The volume between the stopcock and the tip of the braking capillary at the top should be small, and the tip of the pipet should be well constricted in a long capillary (to be immersed). The receiving tube is clamped to a ring stand and a high-speed stirrer is inserted which must not rotate so rapidly that air is entrained.

The concentration cell, which consists of one electrode inside and one outside a pipet (Figure 7, 8), is connected by a single-pole double-throw switch to a 1- to 10-microfarad condenser, and by throwing the switch to the opposite position, the condenser is discharged through a moving-coil galvanometer, whose deflection is proportional to the charge on the condenser and hence to the electromotive force of the concentration cell. The galvanometer is short-circuited by the critical damping resistance. Ten milligrams of dry or freshly dissolved potassium iodide are added to the receiving tube that serves as a titration vessel and the pipet electrode is inserted.

The iodine solution is drawn up into the pipet electrode by means of a rubber bulb about ten times to make sure that the same concentration prevails inside as outside, and this is verified by noting the zero potential. The level inside the cell should always be above the point of the sealing of the platinum wire.

The microburet is filled with 0.001 *N* thiosulfate solution by suction, the capillary is adjusted at the top, the level is brought down to zero, and the tip is carefully washed off before inserting it into the 10-cc. receiving tube which serves as the titration vessel. Then 0.005 cc. of thiosulfate is introduced, the switch is thrown to charge the condenser and after 15 seconds is thrown to the galvanometer, and the deflection is read. Then the pipet is rinsed again, but in this case a standard number of rinsings is sufficient without verifying the zero potential, and the process is repeated. After the galvanometer deflection reaches a maximum, 2 more titration increments are made on the down grade, the results are plotted, and the end point is found by connecting the points of reading. Immediately after the titration a standard containing 0.5 $\gamma$  of iodine as iodate is titrated.

In both these titrations the "potassium iodide blank" in cubic centimeters of thiosulfate is subtracted and the iodine is calculated in the unknown. A "reagent blank" is also run every time any reagents are made up—i. e., distillation is made with the same amount of alkali, rare earth oxide, azide, sulfuric acid, and ferric sulfate as is used in the analysis and with the same amount of bromine water in the receiver. From the resulting titration the "potassium iodide blank," in cubic centimeters of thiosulfate, is subtracted and the iodine in the other "reagents" is calculated.

**ACCURACY OR SENSITIVITY OF THE TITRATION.** Close to the end point of the titration the addition of 0.001 cc. of 0.001 *N* thiosulfate will cause a deflection of many millimeters on the scale of a sensitive galvanometer. Since one division of the buret (0.001 cc.) of 0.001 *N* thiosulfate is equivalent to about 0.02 $\gamma$  of iodate iodine (or the iodine liberated by the action of 0.02 $\gamma$  of iodate iodine on excess iodide) and only 2 points on the titration curve before the end point are necessary, 0.04 $\gamma$  of iodate iodine may be titrated. The authors have found 0.01 to 0.02 $\gamma$  of iodate iodine in 10 mg. of the purest American and British potassium iodide which they have obtained even after recrystallization. Therefore they have not tried to increase the sensitivity by further dilution of the thiosulfate.

## Reagents

**DISTILLED WATER.** All water used should be distilled, made alkaline, and redistilled in a nonmetal still for metals act as oxidation catalysts.

**STANDARD POTASSIUM IODATE,** 1.7835 grams of the recrystallized salt, dried 1 hour at 130° C., dissolved to make 1 liter of solution. This contains about 1058 $\gamma$  of iodine per cc. It should be diluted to a thousand volumes.



**POTASSIUM IODIDE.** A solution of the recrystallized salt containing 10 mg. per cc. is made up just before using and 1 cc. is added to each titration. A blank may be run on 8 or 10 cc. One cubic centimeter should not contain more than 0.02% of iodate iodine.

**STANDARD POTASSIUM IODIDE,** 1.308 grams of the recrystallized salt (dried at 110° C.) per liter. One cubic centimeter of this diluted to 1 liter contains 1% of iodine per cc.

**STANDARD 0.1 N SODIUM THIOSULFATE,** 24.85 grams of the pure crystalline salt and 0.1 gram of sodium carbonate dissolved to make 1 liter of solution. It should be diluted to 0.001 N before use, adding 0.1 gram of sodium carbonate per 100 cc. of diluted solution in a paraffin-lined flask.

**0.1 N SULFURIC ACID,** 0.25 cc. of the pure concentrated acid diluted to 90 cc.

**21 N SULFURIC ACID,** 140 cc. of concentrated acid per 240 cc. of solution.

**BROMINE.** The purest bromine available is purified by washing 3 times with water (iodine goes in water as iodate). Bromine water is prepared by bubbling the bromine vapor through water just before use. One cubic centimeter of bromine water plus 5 cc. of 0.1 N sulfuric acid made up to 9 cc. is about the color of 0.07 per cent dichromate solution and is aerated 30 minutes at 100° C. It should not titrate more than 0.05% of iodate iodine.

**FOUR PER CENT FERRIC SULFATE.** Four grams of crystalline, hydrated ferric chloride are dissolved in 100 cc. of water plus 3 cc. of 6 N sulfuric acid. The solution is evaporated nearly to dryness over a free flame, 100 cc. of water are added, and the operation is repeated. Upon dilution to 100 cc., the solution is filtered if necessary.

**SODIUM AZIDE** (Eastman's or Kahlbaum's), 500 mg. in 100 cc. of water.

**0.1 N SODIUM HYDROXIDE,** 0.4 gram of (c. p.) sodium hydroxide per 100 cc. of solution, in a paraffin-lined bottle. Since it usually contains some carbonate, it is preferably dissolved in an equal weight of water and the carbonate is settled, then it is diluted and titrated with standard acid. It is used in cleaning the electrodes and still and in determining the acidity of the solutions in which iodine is determined.

**RARE EARTH OXIDE,** mixed oxides of lanthanum, cerium, neodymium, praseodymium, and samarium. Since it is difficult to separate these oxides, they are used in this impure form as oxidation catalysts.

## Experimental

Iodine may be concentrated and removed from interfering electrolytes by precipitation as silver or palladium iodide, by extraction of iodide from carbonate solutions with 93 per cent ethyl alcohol, or by extraction of iodine with carbon tetrachloride, but these methods are either inapplicable to 1% quantities of iodine or unduly time-consuming. Therefore distillation (which had been used by McCullagh and by Leipert) was developed as a micromethod accurate for small quantities (0.2 to 10%) of the element.

An attempt to receive iodine vapor in sodium hydroxide plus hydrogen peroxide failed, since hydrogen peroxide cannot be completely destroyed, even by baking the evaporated solution. It may be removed in acid solution, but boiling the acid solution resulted in loss of iodine as hydrogen iodide. In one experiment, hydriodic acid in 8 cc. of water plus 0.625 cc. of 0.1 N sulfuric acid was aerated 10 minutes at 100° C. The loss was 15 to 20 per cent.

TABLE I. MINIMUM QUANTITY OF SODIUM SULFITE TO REDUCE 1% OF IODATE IODINE

0.2% Na <sub>2</sub> SO <sub>3</sub> Cc.	5% NaOH Cc.	6 N H <sub>2</sub> SO <sub>4</sub> Cc.	6% Hydrated Ferric Ammonium Sulfate Cc.	Recovery of Iodine in Receiver %
0.1	1	5	0.5	90.3
0.5	1	5	0.5	99.0
1.0	1	5	0.5	96.4

The iodine might be received in sodium hydroxide, but the blank is augmented by the reagent. It was found most satisfactory to receive the distilled iodine directly in bromine water. No iodine was lost even with the delivery tube at

some distance from the surface of the bromine water, but to be safe, the tip of the condenser was kept just above the level of the oxidant. Steam-distillation of iodine was not nearly as quantitative as air-distillation.

Nitrous acid is a fairly good oxidizer for iodine and possesses the added advantage that it will reduce any hypoiodite or iodate, but it is not dependable for 1% quantities. In fact, it was found necessary to destroy traces of nitrous acid (formed in the alkali fusion of the material) with sodium azide before oxidation of the iodide to iodine.

Obviously, the alkaline solution in the still must be concentrated to small volume before acidification, so as not to overflow the receiver with the distillate. The excess hydrazoic acid may be conveniently removed from the solution by boiling after adding the acid to the still. Ferric iron was found to be the best oxidant for liberating iodine, catching the distillate in bromine water to prevent loss of iodine as hydriodic acid.

Minimal quantities of reagents must be used not only to reduce the blank but to increase the efficiency of removal of iodine. Table I shows the minimum quantity of reducing agent necessary to reduce iodate before the solution is transferred to the still. In this case sulfite was used, but similar results were obtained with azide.

TABLE II. QUANTITY OF ACID USED IN DISTILLATION

(Still charge consisted of 0.5 cc. of saturated sodium carbonate, 0.5 cc. of 0.2 per cent sodium sulfite, 1 cc. of 0.5 per cent sodium hydroxide, 0.2 cc. of 4 per cent ferric sulfate, and 1.1% of iodine as iodide.)

6 N H <sub>2</sub> SO <sub>4</sub>	Recovery of Iodine in Receiver %	Mean %
Cc.		
0.5	50.8	45.8
0.5	40.8	
1.0	64.0	70.4
1.0	76.8	
2.0	66.5	79.7
2.0	99.7	
2.0	59.5	
2.0	93.0	
3.0	89.0	91.5
3.0	93.9	
4.0	88.2	85.6
4.0	82.9	

The data in Table I indicate that 0.5 cc. of 0.2 per cent sodium sulfite is ample to reduce 1% of iodine from iodate to iodide (but this did not reduce all the nitrite), and Table II indicates the optimum amount of 6 N sulfuric acid to be about 3 cc. (After fusion, more acid must be used to neutralize the sodium hydroxide, and 21 N is preferable.)

Ferric sulfate is as efficient as ferric ammonium sulfate as an oxidant (Table III), and is preferable because less electrolyte is introduced. Table III indicates that 0.2 to 0.4 cc. of 4 per cent ferric sulfate should be used.

The volume of water introduced with the acid is important; 6 N sulfuric acid is superior to 3 N, as shown in Table IV.

Finally, the method of distillation is of extreme importance. Some iodine is held by the water which condenses in the trap; this iodine cannot be effectively driven over by adding more water to the still and evaporating nearly to dryness (sulfur trioxide fumes), repeating the process several times, as was done in obtaining the data for Tables I, II, and III. Even with optimum quantities of reagents, the loss still amounts to 5 to 10 per cent. If, however, the trap be heated to prevent condensation at the end of the distillation, the maximum loss of iodine amounts to only 3 per cent (Table V) on inorganic solutions. In the presence of traces of organic matter, however, iodine continued to come over 3 minutes after the appearance of sulfur trioxide fumes with a 5-mm. flame (destroying traces of organic reducing substances by micro-Kjeldahl technic).



TABLE III. COMPARISON OF FERRIC SULFATE WITH FERRIC AMMONIUM SULFATE AS OXIDIZING AGENT

(Still charge consisted of 1.1 γ of iodine as iodide, 0.5 cc. of saturated sodium carbonate, 0.5 cc. of 0.2 per cent sodium sulfite, 1 cc. of 0.5 per cent sodium hydroxide, and 2 cc. 6 N sulfuric acid.)

Oxidant Cc.	Recovery of Iodine in Receiver	
	6.6% ferric ammonium sulfate (hydrated) %	4% ferric sulfate %
0.2	92.5	99.7
0.2	86.7	66.5
0.2		93.0
0.2		59.5
	Mean 89.6	79.7
0.4	83.5	85.5
0.4		85.5
	Mean 83.5	85.5
0.7	84.7	78.0
0.7	84.4	77.2
	Mean 84.6	77.6
1.0	85.0	
1.0	74.2	75.5
	Mean 79.6	75.5

OXIDATION OF IODINE TO IODATE BY BROMINE, AND REMOVAL OF EXCESS OXIDANT. One-half cubic centimeter of saturated bromine water is ample to oxidize 1 to 10γ of iodine to iodate. The excess cannot be removed by treating with formic acid or phenol as in the macrooxidation, because of incompleteness of reaction between formic acid or phenol and bromine. An error of +2 per cent will be introduced in the 10γ titration or +20 per cent in the 1γ titration. Because of the reducing action of hydrazoic acid, 2 cc. of bromine water are used; if this bromine disappears during distillation more bromine water is added.

TABLE IV. DISTRIBUTION OF IODINE IN DISTILLATES

(Still charge consisted of 1.1 γ of iodine as iodide, 0.5 cc. of saturated sodium carbonate, 0.5 cc. of 0.2 per cent sodium sulfite, and 0.2 cc. of 4 per cent ferric sulfate at the proper time.)

Fraction of Distillate	Volume of Fraction Cc.	Total Iodine in Fraction, Acidified with:	
		6 cc. of 3 N H <sub>2</sub> SO <sub>4</sub> fraction %	3 cc. of 6 N H <sub>2</sub> SO <sub>4</sub> fraction %
1st	2	15.0	54.1
2nd	2	48.3	37.0
3rd	2	25.3	8.9
4th	2	11.4	0.00

Iodic acid is perfectly stable at 100° C. for 30 minutes or more. Aeration of the acidified solution at 100° C. may therefore be used.

One-half microgram of iodine as iodate was put in each of 4 tubes, and to it were added 1, 5, 5, and 7.5 cc., respectively, of 0.1 N sulfuric acid. Tube II was used as standard and tubes I, III, and IV were made up to 9 cc. and aerated at 100° C. for 30 minutes. Tube I titrated 0.5γ, tube III 0.5γ, and tube IV 0.504γ of iodine.

In order to determine the "bromine blank," 2 series of 4 titrations each were made on acidified bromine water alone. In the first series the total bromine added was constant, but the aeration of the first was so great as to break bubbles at the top of the tube, and the others progressively decreased. The titrations were 0.0045, 0.0048, 0.0045, and 0.005 cc. of thiosulfate. In the second series the aeration was constant, but the quantity of bromine water was 1/9, 2/9, 3/9, and 4/9 of the amount required to match 0.07 per cent potassium bichromate solution. The titers were 0.0044, 0.0042, 0.0045, and 0.0042 cc. of thiosulfate. If the aeration is not performed in a hood it is necessary to open the windows before titrating. The bromine blank is not due to iodine in the 0.1 N sulfuric acid, since a series of 3 brominated tubes with 1, 2, and 5 cc. of this acid titrated 0.004, 0.0045, and 0.0045 cc. of thiosulfate.

The presence of sodium sulfate retards the removal of bromine, so that it is not practical to receive the iodine in hypobromite and then add sulfuric acid.

MICROTITRATION OF IODINE. Small quantities of iodine may be determined gravimetrically by precipitation as silver

or palladium iodide, but this method is not sufficiently sensitive for 1 to 10 micrograms of the element. The titration of iodide ion with mercuric chlorate or with silver nitrate, using a silver-silver iodide electrode, also lacks sensitivity. Most schemes for the determination of 1 to 10γ of iodine oxidize the element with bromine water to iodate by the Winkler technic, since six times the original quantity of iodine becomes available for titration upon addition of potassium iodide to the iodate. Sodium thiosulfate is the most useful reducing solution for the titration of the free iodine, but the use of starch as indicator for this determination introduces error, since an appreciable amount of iodine (at least 0.05γ in 2 cc.) is required to give the final faint blue color to the starch. In this research an electrometric method has been modified for titration of the small volumes of solution encountered.

TABLE V. COMPARISON OF METHODS OF DISTILLATION

(Still charge consisted of 1.1 γ of iodine as iodide, 0.5 cc. of saturated sodium carbonate, 0.5 cc. of 0.2 per cent sodium sulfite, 1 cc. of 0.5 per cent sodium hydroxide, 3 cc. of 6 N sulfuric acid, and 0.2 cc. of 4 per cent ferric sulfate.)

Method	Error Per Cent of Total Iodine
Distill to sulfur trioxide fumes	
Flaming trap only at termination of distillation	-3.5
Flaming trap constantly during distillation	Av. 0.0, -2.8, +0.2, -2.4 -1.2

The dead-stop end-point method of Foulk and Bawden (1) was proved unsatisfactory. The differential method of MacInnes (10), using the pipet electrode of Hall, Jensen, and Baekström (2) (but reduced to 0.1-cc. volume), gave satisfactory results, providing the electrode potential was used to charge the condenser and discharged through the galvanometer. The platinum wire must not be too small and must be heated to a white heat after bending into shape.

The titration solution should be vigorously stirred, but the entrainment of air is undesirable, since some iodide may be oxidized by it to iodine.

When more than 5γ of iodine (as iodate) are to be titrated, the electrodes may be kept out of the solution until all but about 1γ of the iodine has been reduced, otherwise the high iodine concentration may polarize the electrodes. Tenth-normal sodium hydroxide may be used to clean them even during the titration if the end point has not been approached, but the galvanometer deflections observed before cleaning the electrodes cannot be used in plotting the end point.

In titration of 1γ of iodine as iodate, the volume of the solution should not be greater than 10 cc. As regards acidity of an iodine solution during thiosulfate titration, Kolthoff and Furman (3) give the following requirements:

	pH
0.1 N iodine	< 7.6
0.01 N iodine	< 6.5
0.001 N iodine	< 5

On plotting these pH values against concentration, we find in extrapolation to 0.000004 N solution a pH of around 2 is required. It was found empirically (Table VI) that a pH of 2.2 was most satisfactory. One cubic centimeter of 0.0625 N sulfuric acid added to make 10 cc. of final solution to be titrated will approximate this pH, but it is possible to titrate in the presence of 5 cc. of 0.1 N sulfuric acid. A potassium iodide solution containing 12.5 mg. per cc. was prepared, and 1 cc. of it was added to the acidified solution of iodate. The total volume of 10 cc. was determined by a mark on the tube. The completeness of the reduction of iodate depends both on the potassium iodide and acid concentration (Table VIII). For titration of 10γ of iodine as



iodate, a 35-cc. volume was maintained for the solution to be titrated, and 2 cc. of the sulfuric acid and 2 cc. of the potassium iodide solution were added.

The buret used in titration was 0.1 cc., graduated in thousandths and with stopcock and air capillary at top, according to Lochte and Hoover (4).

TABLE VI. EFFECT OF ACID AND IODIDE CONCENTRATION ON TITRATION OF 1γ IODINE AS IODATE

0.0625 N H <sub>2</sub> SO <sub>4</sub> Cc.	KI (12.5 mg. per cc.) Cc.	End Point Approximately 0.001 N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Cc.	Type of Curve <sup>a</sup>
0.2	0.2	0.0574	Fair
0.2	0.6	0.0595	Good
0.2	1.0	0.0625	Good
0.2	1.4	0.0630	Excellent
0.6	0.2	0.0570	Good
0.6	0.6	0.0623	Good
0.6	1.0	0.0624	Good
0.6	1.4	0.0615	Excellent
1.0	0.2	0.0550	Poor
1.0	0.6	0.0600	Fair
1.0	1.0	0.0625	Good
1.0	1.4	0.0625	Excellent
1.4	0.2	0.0538	Poor
1.4	0.6	0.0555	Poor
1.4	1.0	0.0613	Good
1.4	1.4	0.0627	Excellent

<sup>a</sup> A poor curve refers to a relatively flat one, where the inflection point cannot be conclusively established.

Thousandth-normal sodium thiosulfate is a convenient strength to use, since 1γ of iodine as iodate requires about 0.005 cc., or about half the capacity of the buret. The sodium thiosulfate is prepared by dilution of 0.1 N solution. Table VII indicates the added stability afforded the dilute solution by addition of 0.1 gram of sodium carbonate per 100 cc. Nevertheless, it should always be standardized just before use or at intervals, and a time curve should be drawn.

TABLE VII. EFFECT OF ADDED SODIUM CARBONATE

Approximate Normality of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Time Minutes	Fading %
0.0015	33	2.0 ?
	67	1.45
	309	4.35
	1860	13.1
0.001	30	3.3
	65	4.65
	305	6.0
	1860	6.8
0.0005	25	0.6
	61	1.2
	300	2.7
	1860	11.4
0.0005 + 0.1 gram of Na <sub>2</sub> CO <sub>3</sub> per 100 cc.	220	0.8
	1740	4.1

With such a small buret, the sodium thiosulfate cannot be added to the iodine solution fast enough to endanger precipitation of sulfur unless the acidity is very high, but it may be best to have the acidity of the standard equal to that of the unknown. Uniform increments should be added, for unequal increments near the end point necessitate an additional calculation. It was found that 0.005-cc. increments gave more reproducible results than 0.0025-cc. increments (Table VIII). In titration of very small quantities of iodine, smaller increments are imperative.

Since in some analyses hydrochloric acid (from chlorides) equivalent to about 3.5 cc. and sulfur trioxide equivalent to about 1.5 cc. of 0.1 N sulfuric acid are distilled, the effect of 5 cc. of 0.1 N sulfuric acid on the titration was studied and the type of curve was found to be excellent.

Eight rinses of the electrode pipet may be required before adding the next increment of the sodium thiosulfate, and

after adding the increment 15 seconds should elapse between throwing the switch to charge the condenser and reading the voltage.

The reproducibility of titration is 2 per cent (Table VIII).

The potassium iodide solution should be made fresh, as a sample that had stood 3 days increased its "iodate iodine" content from about 0.01γ per cc. to 0.074γ per cc. Since the total blank on all the reagents should not be more than about 0.08γ, and 1 cc. of potassium iodide solution is used in an analysis, it is imperative to use fresh potassium iodide solution.

TABLE VIII. TITRATION OF 1γ OF IODINE AS IODATE

0.005-Cc. Increments of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>		0.0025-Cc. Increments of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	
End point Cc.	Variation from average	End point Cc.	Variation from average
0.0565	+0.7	0.0542	-2.3
0.0558	-0.5	0.0570	+2.7
0.0570	+1.6	0.0568	+2.3
0.0560	-0.2	0.0540	-2.7
0.0554	-1.3	....	...
Av. 0.0561		0.0555	

There are at least three sources of substances that might augment the amount of iodine in this analysis: the iodide in the reagents used, the bromine remaining after aeration, and the iodate iodine in the potassium iodide used in titration. Therefore a blank must be subtracted from the result.

Accuracy of the Method

Two hundred cubic centimeters of chlorinated tap water plus 0.1 gram (1 pellet) of sodium hydroxide were evaporated to a small volume, transferred to a nickel crucible, and evaporated to dryness, 0.5 gram of sodium hydroxide was added, and the material was fused. Water was added to dissolve the fusion and 2 mg. of sodium azide were added. This was transferred to the still and together with a similar sample to which 0.54γ of iodine had been added, analyzed with an error of 2 per cent (Table IX). Two hundred cubic centimeters of deep-well water plus 0.1 gram of sodium hydroxide plus 2 mg. of sodium azide were evaporated to small volume and transferred to a nickel crucible, 0.5 gram of sodium hydroxide was added, and the material was fused, transferred to the still, and, together with a similar sample to which 0.55γ had been added, analyzed with an error of 2 per cent (Table IX).

TABLE IX. ANALYSIS OF NATURAL AND CHLORINATED TAP WATER AND URINE

	Iodine in Sample γ	Iodine Added γ	Total Iodine γ	Differ- ence γ	Error %
200 cc. of Minneapolis tap water	0.43	0.54	0.98	0.55	2
200 cc. of LaGrange deep- well water	0.59	0.55	1.13	0.54	2
2.5 cc. of urine	0.975	..	..	..	..
5 cc. of urine	1.95	0.5	2.44	0.49	2

Urine (2.5 cc. plus 0.1 gram of sodium hydroxide plus 2 mg. of rare earth oxide) was evaporated in a nickel crucible to dryness; 0.9 gram of sodium hydroxide was added and fused; the material was dissolved in water, 2 mg. of sodium azide were added, and this, together with a similar sample of 5 cc. of the urine and a third sample of 5 cc. of the urine plus 0.5γ of iodine, was analyzed with a recovery of 98 per cent (Table IX). The urine was from a person taking iodized salt.

Summary

After boiling the sample in alkaline solution (which hydrolyzes many compounds) and fusing with alkali with rare earth oxides as catalysts (which decomposes urea, evaporates ammonia, and begins the process of oxidation), the iodine may be freed by micro-Kjeldahl combustion in 4 minutes. Iodate is reduced and nitrite destroyed with azide. During the



micro-Kjeldahl combustion the iodide is oxidized to iodine by ferric iron and distilled into bromine water which oxidizes the iodine to nonvolatile iodate. The excess bromine is blown out with a current of air at 100° C. After adding 10 mg. of potassium iodide, the iodine is titrated with thiosulfate, using an electrometric method to determine the end point.

The method is applicable to drinking water, soil solution, urine, thyroid gland, seaweed, sponge, and many other substances, where a sample containing 0.2% of iodine contains only small quantities of organic matter (other than urea), silica, or halides.

The method may be used to titrate accurately 0.04 microgram of iodine, but a blank of about 0.02% must be subtracted on account of the potassium iodide. Blanks must be subtracted on account of the reagents used in the fusion, distillation, and bromination of the sample.

The electrometric titration is adapted to smaller quantities of iodine than heretofore. The distillation is performed with smaller additions of reagents than in previous methods. The method is shorter and less expensive than combustion tube methods.

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# The Use of Trautz's Micro-Dumas Method with the Apparatus of Pregl

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A MICRO-DUMAS method has been described by Trautz in which the combustion products are swept out at the rate of four bubbles per second (1, 3, 4). This rate is more than four times that recommended by Pregl (2); the time required for a complete analysis is thus reduced to only a half hour. Trautz offered no analytical data other than an analysis of acetanilide, and carried out this analysis with apparatus in which the parts were connected by ground-glass joints.

TABLE I. TYPICAL RESULTS

	Nitrogen Found %	Nitrogen Calculated %
Azobenzene (C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> )	15.32	15.38
p-Bromoacetanilide (C <sub>8</sub> H <sub>8</sub> OBrN)	6.65	6.58
2,4-Dinitrophenylhydrazine (C <sub>6</sub> H <sub>6</sub> O <sub>4</sub> N <sub>4</sub> )	28.18	28.28
Phenylurea (C <sub>7</sub> H <sub>8</sub> ON <sub>2</sub> )	20.63	20.59
Threonine (C <sub>4</sub> H <sub>9</sub> O <sub>3</sub> N)	11.71	11.76
N-Methyl-N,N'-diethyl-N-phenyltrimethylenediamine (C <sub>14</sub> H <sub>24</sub> N <sub>2</sub> )	12.72	12.72
tert-Butylglyoxal-2,4-dinitrophenylhydrazone (C <sub>12</sub> H <sub>14</sub> O <sub>6</sub> N <sub>4</sub> )	19.19	19.05
Benzoylmethionine (C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> NS)	6.05	5.97
Flavone-2,4-dinitrophenylhydrazone (C <sub>21</sub> H <sub>14</sub> O <sub>5</sub> N <sub>4</sub> )	13.85	13.91
5,5'-Methylallylethylmalonylurea (C <sub>10</sub> H <sub>14</sub> O <sub>3</sub> N <sub>2</sub> )	13.40	13.33
Methylvaline (C <sub>6</sub> H <sub>13</sub> O <sub>2</sub> N)	10.68	10.68
2-Phenyl-4-benzoylpyrrole (C <sub>17</sub> H <sub>15</sub> ON)	11.50	11.57
4,4'-bis-[N-(α,α'-dimethyl-β-carbethoxy)-pyrrole]-3,3'-dimethylbiphenyl (trans) (C <sub>22</sub> H <sub>26</sub> O <sub>4</sub> N <sub>2</sub> )	5.32	5.46
Phenylhydrazone of tetramethoxygossypol (C <sub>46</sub> H <sub>50</sub> O <sub>4</sub> N <sub>2</sub> )	7.40	7.43
N,N'-(p,p'-[N-(2-hydroxy-1-propyl)-benzenesulfonamide]]-glutaramide (C <sub>23</sub> H <sub>27</sub> O <sub>5</sub> N <sub>4</sub> S <sub>2</sub> )	10.04	10.07
Sodium phenylsulfamate (C <sub>6</sub> H <sub>5</sub> O <sub>2</sub> NNaS)	7.14	7.17

Experience in this laboratory has shown that it is possible to use this method with a slightly modified Pregl apparatus and that the method is applicable to a wide variety of compounds containing nitrogen. A complete analysis requires an average time of 30 minutes.

The following changes were made in Pregl's apparatus:

The tubing which joined the azotometer tip and the combustion tube tip, and the stopper at the end of the combustion tube were the only rubber connections used. The others were eliminated by sealing the joints together, in order to reduce the possibility of leakage.

A ball-and-socket ground-glass joint was made between the azotometer tip and the combustion tube tip. This was done by widening the former slightly, heating the latter in a flame until a thick wall was formed, and then grinding the two tips together with silicon carbide. A trace of vaseline was used in the joint. The tips were connected as usual with impregnated microtubing. The ground-glass joint was made to lessen the possibility of losing nitrogen at that point.

An electric furnace was used to maintain the permanent filling at 750° C. It was found that at this temperature no carbon monoxide passes through the combustion tube without being oxidized.

An asbestos tent was suspended over the wire gauze and moved forward with gauze and burner. The tent was used to facilitate a rapid and complete combustion.

Typical results from about 250 analyses are given in Table I (Pregl's 2 per cent correction was used throughout).

## Acknowledgment

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# Relative Value of Certain Azo Derivatives of 8-Hydroxyquinoline as Analytical Reagents

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This paper continues a study begun by Gutzeit and Monnier, on the development of specific spot paper and spot plate analytical reagents, and reports the effect of eighteen azo derivatives of 8-hydroxyquinoline on nearly all the metals except the alkali, alkaline earth, and most of the rare earth metals.

Test reagents were saturated alcoholic solutions of the dyes, and test solutions contained 3 mg. of active constituent per ml. of 20 per cent nitric acid solution. In a few cases 20 per cent aqua regia and hydrochloric acid were employed.

The following derivatives of 8-hydroxyquinoline gave specific tests for the metals indicated: (I) 5-(2-hydroxyphenylazo)-,

Pd<sup>++</sup>; (II) 5-(3-hydroxyphenylazo)-, Hg<sup>++</sup>, Pd<sup>++</sup>; (VI) 5-(2-chlorophenylazo)-, Pd<sup>++</sup>; (VII) 5-(3-chlorophenylazo)-, Hg<sup>++</sup>, Pd<sup>++</sup>; (VIII) 5-(4-chlorophenylazo)-, Hg<sup>++</sup>; (X) 5-(3-tolylazo)-, Hg<sup>++</sup>, Pd; (XII) 5-(4-arsenophenylazo)-, Hg<sup>++</sup>; (XV) 5-(8-hydroxy-3,6-disulfo-1-naphthylazo)-, Hg<sup>++</sup>; (XVI) 5-(benzidine-monoazo)-, Pd<sup>++</sup>, VO<sub>2</sub><sup>+</sup>, or VO<sub>3</sub><sup>-</sup>.

In practically all cases chloride ion obscures the test, but tartrate ion has, in general, no effect. This series of dyes does not give specific tests for copper, nickel, and molybdenum as MoOCl<sub>5</sub><sup>-</sup> ion. Only a few dyes give specific tests for mercury and palladium which may be distinguished by the fact that hydrochloric acid destroys all tests for mercury.

A STUDY was made by Gutzeit and Monnier (2) of the effect of practically all the metals of the periodic table, except the alkali and the alkaline earth metals, on a series of sixteen azo derivatives containing the functional group 8-hydroxyquinoline. Consideration was given to the correlation of structure and specificity of the dyes. From their research, Gutzeit and Monnier have concluded that:

1. Except for a few minor and scattered reactions with various cations, the azo dyes containing the 8-hydroxyquinoline nucleus seem to give consistent reactions which are specific for mercury, copper, palladium, nickel, and molybdenum as MoOCl<sub>5</sub><sup>-</sup>.
2. The tests should be carried out in acid solution.
3. Certain anions such as tartrate and chloride obscure the results.
4. Polar groupings para to the point of coupling on the aromatic nucleus tend to increase the positiveness of the test.
5. A reagent with a given specific grouping, as the azo-8-hydroxyquinoline group, does not acquire new reactions with

new ions by substitution with different radicals, but the sensitivity and specificity of a given reagent can be improved by introducing other substituents without modifying the reactions of the functional group.

Some new azo derivatives of 8-hydroxyquinoline were prepared by Bennett and Shreve (1). The relative value of these dyes as analytical reagents was studied.

## Experimental

Because of the low solubility of the dyes in the common solvents, it was necessary to prepare saturated solutions. Ninety-five per cent ethyl alcohol was chosen as the solvent because it provides a homogeneous phase with the dye and the test solutions. Other solvents which would provide mutual solubility such as absolute ethyl alcohol and ethylene glycol were considered, but when the solubility of the dyes in these solvents was studied (1) it was observed that no particular advantage would be gained by their use.

TABLE I. REACTION OF DYES WITH SOLVENTS

No.	20% Nitric Acid		20% Hydrochloric Acid		20% Aqua Regia	
	Spot paper	Spot plate	Spot paper	Spot plate	Spot paper	Spot plate
I	No change	RO spot	No change	RO spot	Dye bleached	Dye bleached
II	Pink stain	RO spot	RO stain	OR spot	Dye bleached	RO spot
III	ROT2 ring	ORT1 spot	ROT2	ORT1 spot	Dye bleached	RT2 spot
IV	Dye bleached	No change	Dye bleached	No change	Dye bleached	Dye bleached
V	Dye bleached	OYT1 spot	Dye bleached	OYT1 spot	Dye bleached	Dye bleached
VI	Dye bleached	No change	Dye bleached	No change	Dye bleached	Dye bleached
VII	Dye bleached <sup>a</sup>	No change	YOT2 spot	No change	Dye bleached	Dye bleached
VIII	Dye bleached	YOT2 spot	Dye bleached	YOT2 spot	Dye bleached	Dye bleached
IX	No change	YT2 spot	No change	YT2 spot	Dye bleached	Dye bleached
X	OT2 spot	RO spot	OT2 spot	RO spot	Dye bleached	Dye bleached
XI	Dye bleached <sup>a</sup>	OYS1 spot	Dye bleached <sup>a</sup>	OYS1 spot	Dye bleached	Dye bleached
XII	Dye bleached	OY spot <sup>b</sup>	Pink spot	OY spot <sup>b</sup>	Dye bleached	Dye bleached
XIII	Dye bleached	OT2 spot	Dye bleached	OT2 spot	Dye bleached	Dye bleached
XIV	VRT2 ring	RT2 spot	VRT2 ring	RT2 spot	Violet ring	Dye bleached
XV	Cinnamon spot	YO spot	Cinnamon spot	YO spot	OT1 spot	YO spot
XVI	Orange ring	OYS1 spot	Orange ring	OYS1 spot	Bright O ring <sup>c</sup>	Orange spot
XVII	No change	.....	No change	.....	No change	.....
XVIII	No change	.....	No change	.....	No change	.....

<sup>a</sup> Slightly. <sup>b</sup> Faint. <sup>c</sup> Then greenish fugitive ring, changing to yellow spot.

O = orange; R = red; Y = yellow; V = violet; T = tint; S = shade (3).

Test solutions were prepared, such that each milliliter of solution contained 3 mg. of metallic group. Twenty per cent chloride-free nitric acid, hydrochloric acid, and aqua regia were employed as solvents. The substances dissolved in 20 per cent nitric acid were Th(NO<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Hg(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, AgNO<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O, Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Rh(NO<sub>3</sub>)<sub>3</sub>, Pd(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Ti(NO<sub>3</sub>)<sub>3</sub>, Cs(NO<sub>3</sub>), Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and V<sub>2</sub>O<sub>5</sub>; those in 20 per cent aqua regia were OsO<sub>4</sub>, IrCl<sub>3</sub>, and Ru(NO)Cl<sub>3</sub>; and those in 20 per cent hydrochloric acid were As<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, and MoO<sub>3</sub>.



In solution, molybdenum trioxide was transformed into the anion  $\text{MoOCl}_5^{--}$  (2) by dissolving the substance in 20 per cent hydrochloric acid, boiling the solution, and evaporating almost to dryness. Then 10 ml. of 20 per cent hydrochloric acid were added, and the solution was concentrated to about half the volume, cooled, and diluted in a volumetric flask to 50 ml. with 20 per cent hydrochloric acid.

Procedure

In analysis by the spot paper test, one drop of the alcoholic solution of the test reagent is placed on a piece of good quality filter paper and allowed to stand a moment. Then a drop of the test solution is placed on the center of the reagent spot. [In studying the effect of interfering anions, a drop or fraction thereof of the test solution of such an ion (chloride or tartrate) is placed on the reagent spot or drop before or after a drop of the test solution as desired. A solvent blank is used as a control.]

In analysis by spot plate tests, two drops of the test reagent are placed in a well of a porcelain spot plate. To this a drop of test solution is added.

Dilution tests are made by measuring a quantity of standard test solution and diluting by the proper solvent to a definite volume.

In the analysis of an unknown (2), the sample for analysis is dissolved in concentrated nitric acid and the solution evaporated to dryness. The residue is taken up in about 20 per cent nitric acid for use in spot paper or spot plate tests.

Data

The following dyes were studied in this investigation and are referred to by number in the discussion below:

- I. 5-(2-hydroxyphenylazo)-8-hydroxyquinoline
- II. 5-(3-hydroxyphenylazo)-8-hydroxyquinoline
- III. 5-(2-nitrophenylazo)-8-hydroxyquinoline
- IV. 5-(3-nitrophenylazo)-8-hydroxyquinoline
- V. 5-(4-nitrophenylazo)-8-hydroxyquinoline
- VI. 5-(2-chlorophenylazo)-8-hydroxyquinoline
- VII. 5-(3-chlorophenylazo)-8-hydroxyquinoline
- VIII. 5-(4-chlorophenylazo)-8-hydroxyquinoline
- IX. 5-(2,5-dichlorophenylazo)-8-hydroxyquinoline
- X. 5-(3-tolylazo)-8-hydroxyquinoline
- XI. 5-(2,6-dimethylphenylazo)-8-hydroxyquinoline

- XII. 5-(4-arsonophenylazo)-8-hydroxyquinoline
- XIII. 5-(3-sulfophenylazo)-8-hydroxyquinoline
- XIV. 5-(1-sulfo-2-naphthylazo)-8-hydroxyquinoline
- XV. 5-(8-hydroxy-3,6-disulfo-1-naphthylazo)-8-hydroxyquinoline
- XVI. 5-(benzidinemonoazo)-8-hydroxyquinoline
- XVII. 5,5'-(benzidinedisazo)-8-hydroxyquinoline
- XVIII. 5-(3,3'-dimethoxybenzidinemonoazo)-8-hydroxyquinoline

The nitrates of aluminum, bismuth, cadmium, cerium, cesium, chromium, lead, magnesium, manganese, rhodium, silver, thallium, thorium, yttrium, zinc, and zirconium, and the chlorides of antimony and arsenic give negative tests with all the dyes. Ruthenium nitroschloride and uranyl nitrate give negative tests also. Molybdenum does not give tests which are of analytical significance. Copper gives mediocre tests with dyes II and X.

Nickel gives mediocre spot paper tests with IV, VII, VIII, and X. Mercury and palladium give tests with VIII, which may interfere with the test with nickel. Osmium gives no tests, and iridium gives a useless test with II. On spot paper cobalt gives very doubtful tests with II, X, and XIII. Iron gives identical results with all the dyes on spot paper, but the color change is so fugitive that the tests are of no value. In both spot paper and spot plate tests, dichromate ion gives excellent results with all the dyes except XVII and XVIII. In certain spot plate tests, the addition of hydrochloric acid after the test drop enhances the significance of the results.

Specific Tests

MERCURY. With II, mercury gives a "violet-red" spot paper stain which is destroyed if treated with hydrochloric acid. On a spot plate, a "red-violet shade two" precipitate (3), which is soluble in hydrochloric acid, forms immediately. This test is similar to that for palladium except that the precipitate or stain formed with palladium is insoluble in hydrochloric acid.

A "red-violet tint two" spot of excellent intensity develops slowly on spot paper with VII. An "orange-red tint one" color develops immediately on a spot plate, and a "violet-red tint

TABLE II. REACTIONS OF METALS WITH DYES

Dye No.	Metals					Co <sup>++</sup>	Fe <sup>+++</sup>	Cr <sub>2</sub> O <sub>7</sub> <sup>--</sup>	Test
	Hg <sup>++</sup>	Cu <sup>++</sup>	Pd <sup>++</sup>	Ni <sup>++</sup>	MoOCl <sub>5</sub> <sup>--</sup>				
I	GY, r: E ORS2, s: D	RO, r: C ROS2, s: B	GY, r: A VRT1, s: A	Neg. Neg.	O, r: D Neg.	GO, s, r: D YOS2, s, f: D	Gr, r, f: D YGRS2, s, f: E	RO, r: A VRT2, s: A	Paper Plate
II	VR, s: A RVS2, s: A	RVS1, r: B RT1, s: C	RVS2, r: A RVS2, p: A	RT1, r, f: C Neg.	YOS1, r: C VBS1, s: C <sup>+</sup>	O, r: C BrGr, p: A	GY, s, f: D <sup>+</sup> GY, r, f: C	VR, s: A VR, s: A <sup>+</sup>	Paper Plate
III	Neg. RT1A, s: C	Neg. Neg.	Neg. .....	Neg. .....	Neg. .....	GY, r, f: D Neg.	GY, s, f: D Neg.	Neg. .....	Paper Plate
IV	OY, r, f: D OT1, s: D	Neg. Neg.	ORT1, r: C RT1, s: B	YOT1, r: B Neg.	Neg. Neg.	Y, r, f: D Neg.	GY, r: B GY, s, f: D <sup>+</sup>	VR, s: B VRT1, s: Aa	Paper Plate
V	Neg. ROT2, s: D	Neg. Neg.	OT2, s: C RT2, s: B	Neg. Neg.	Neg. .....	Neg. .....	Neg. .....	V, s: B VRT1, s: Aa	Paper Plate
VI	Neg. O, s: C	Neg. Neg.	VS2, r: B V, s: A	Neg. Neg.	Neg. .....	GY, r: D YG, s, f: C <sup>+</sup>	GY, s, f: D <sup>+</sup> Neg.	VRT2, r: D RT1, s: Aa	Paper Plate
VII	RVT2, s: A VRT2, p: B	OT2, s, r: C RO, s: E	VRS1, s: C RT1, p: A	ORT2, r: B Neg.	Neg. VRT2, r: B	GY, r: D YOS1, s, f: C <sup>+</sup>	GY, s, f: D <sup>+</sup> Neg.	VRT2, r: A RT1, s: A <sup>+</sup>	Paper Plate
VIII	ORT2, s: B ORT1, s: A	Neg. Neg.	ORT2, r: C RT1, s: B	ORT2, r: B Neg.	Neg. Neg.	YGT2, r, f: D Neg.	GY, s, f: C YS2, s, f: B <sup>+</sup>	ORT2, r: A R, s: Aa	Paper Plate
IX	Neg. OT2, s: D	Neg. Neg.	Neg. .....	Neg. .....	Neg. .....	Neg. .....	GY, s, f: D Neg.	Neg. .....	Paper Plate
X	VR, s: A RS2, s, p: A	VRT1, s: B Neg.	BR, s: C RS2, p: A	RS1, r: B Neg.	VRT1, s: D B', r: C	GY, r, f: D YG, s, f: D <sup>+</sup>	OY, r: B Neg.	VRT1, s: A OR, s: A	Paper Plate
XI	OY, r, f: D YO, s: D	O, r, f: D Neg.	RT2, s: B V, p: B <sup>+</sup>	YO, r, f: D Neg.	Neg. .....	GY, r: C Neg.	GY, r: C GY, s, f: D <sup>+</sup>	RT2, r: C RT1, s: A <sup>+</sup> a	Paper Plate
XII	OT1, r: B OR, p: A	ROT1, r: D Neg.	VRT1, s: A OR, s: A <sup>+</sup>	ROT2, r, f: E Neg.	ORT2, r, f: E Neg.	OT2, r, f: D V, s, f: E	OT1, r: D Neg.	VRT2, s: A VRT1, s: A <sup>+</sup> a	Paper Plate
XIII	ORT2, r, f: B ORT2, s: B	RVT2, r: D OT2, s: E	VRT2, r: D OT1, s: B	ORT2, r, f: D Neg.	Neg. Neg.	Neg. .....	O, r, f: D Neg.	RT2, s: C RVT2, s: B <sup>+</sup>	Paper Plate
XIV	Neg. VRT1, s: C	Neg. VRT1, s: D	VT1, r: C RVBT, s: C	RVT1, r: E Neg.	Neg. Neg.	Neg. .....	BT2, r, f: E B', s, f: C <sup>+</sup>	Neg. .....	Paper Plate
XV	RVT1, s: A VR, s, p: B	Neg. Neg.	Neg. Neg.	Neg. Neg.	Neg. Neg.	Neg. Neg.	Neg. .....	VT2, s: A VR, s: C <sup>+</sup> a	Paper Plate
XVI	B'T2, s: A RVT1, s, p: B	VBT2, r, f: E Neg.	RVT2, s: C YOS1, p: A	VT2, r, f: D Neg.	Neg. .....	YGT1, s: A YS1, s: A	RVT2, s, f: D Neg.	G, s, r: B OG, s: B	Paper Plate
XVII	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Paper Plate
XVIII	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Neg. .....	Paper Plate

R = red; O = orange; Y = yellow; G = green; B' = blue; V = violet; Br = brown; Gr = gray; S = shade; T = tint (3).  
r = ring; s = spot; f = fugitive; p = precipitate; + = tartrate obscures; a = hydrochloric acid enhances.  
Grade rating of tests: A = excellent; B = good; C = fair; D = poor; E = very poor.



TABLE III. LIMIT OF DETECTION

(Milligrams per milliliter of solution)

Dye No.	Mercury		Palladium		MoOCl <sub>5</sub> --		Copper		Vanadium		Cr <sub>2</sub> O <sub>7</sub> --	
	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop
I	3	1	0.1	0.1	+	+	0.3	+	0.3	3	0.3	0.1
II	0.3	0.1	0.1	0.1	3	3	0.3	+	0.3	0.3	0.3	0.1
III	0.3	3	+	+	..	+	..	+	0.3	+	+	1 <sup>a</sup>
IV	1	0.5	0.3	0.3	..	+	..	+	3	+	0.3 <sup>a</sup>	0.3 <sup>a</sup>
V	1	0.5	0.1	0.1	..	+	..	+	+	3	0.3 <sup>a</sup>	0.3
VI	+	3	0.1	0.3	..	+	..	+	0.3	3 <sup>b</sup>	+	0.3 <sup>a</sup>
VII	0.3	0.5	0.1	0.1	..	+	+	1	0.3	3 <sup>b</sup>	+	0.3 <sup>a</sup>
VIII	1	0.5	0.1	0.1	..	+	..	+	+	0.3	0.3-0.1 <sup>a</sup>	0.3 <sup>a</sup>
IX	+	+	+	0.3	..	+	..	+	+	..	+	0.3
X	0.5	0.5	0.1	0.1	3	+	0.3	+	0.3	3	0.3-0.1 <sup>a</sup>	0.3-0.1
XI	+	3	0.3	0.3	..	+	..	+	0.3	..	0.3	0.3-0.1
XII	0.5-1	3	0.1	0.3-0.1	3	3	0.3	0.3	0.3	..	0.3 <sup>a</sup>	0.3 <sup>a</sup>
XIII	3	3	0.3-0.1	0.3	..	+	..	+	+	..	+	0.3 <sup>a</sup>
XIV	3	3	0.3	0.1	1	+	0.3	0.3	0.3	..	+	0.1
XV	0.5-1	0.3	+	3-1	..	+	..	+	+	3	0.3	0.3
XVI	0.3	0.1	0.3	0.3-0.1	..	+	0.3	1	0.3	0.3-0.1	0.3	0.3

<sup>a</sup> HCl added after test drop. <sup>b</sup> Fugitive. + = Negative test obtained with 3 mg. per ml. concentration.

two" precipitate forms, both of which are destroyed by hydrochloric acid. This latter fact serves to distinguish mercury from palladium.

On a spot paper, an "orange-red tint two" spot with a fugitive ring of the same color forms with VIII. An "orange-red tint one" spot, the color of which is destroyed by hydrochloric acid, forms immediately on a spot plate. This is a good test, but the spot plate test is probably the better. Palladium gives a test with the dye too, but the two metals may be distinguished readily.

A "violet-red" spot forms on spot paper immediately with X. On a spot plate a "red shade two" spot forms, and a precipitate settles out. If hydrochloric acid is added to the spot paper or spot plate test, the color or the precipitate is destroyed. This fact serves to distinguish mercury from palladium.

On spot paper, XII forms an "orange tint one" ring which is destroyed by hydrochloric acid. An "orange-red" precipitate which is soluble in hydrochloric acid forms when a spot plate test stands about a minute. This test is characteristic for mercury; probably the spot plate test is the better. Copper may interfere with the test.

A "red-violet tint one" spot forms immediately on spot paper with XV. On a spot plate, a "violet-red" spot forms immediately, and a precipitate of the same color settles out. In both tests hydrochloric acid destroys the color and the precipitate.

**PALLADIUM.** A marked "olive-green" spot which changes to an "olive-green" ring around a pink spot forms on spot paper with I. On standing, the ring turns to a purple color. On a spot plate, a brownish gray precipitate settles out immediately from a "violet-red tint one" spot. Hydrochloric acid causes a part of the precipitate to dissolve, and the mother liquor to assume an orange color.

Palladium gives the same reaction as mercury with II, both on spot paper and on a spot plate. The only way to distinguish palladium from mercury is by the behavior of the spot on paper or spot plate tests towards hydrochloric acid. With palladium, hydrochloric acid has no effect, but with mercury the test is destroyed.

On a spot plate, an "orange shade one" spot forms with VI, and a brown precipitate deposits immediately, which, on standing, assumes a violet or purple color. The precipitate is somewhat soluble in hydrochloric acid.

On a spot plate, a "red tint one" spot, from which a purple precipitate settles, forms immediately with VII. Hydrochloric acid destroys the color of the spot and causes the color of the precipitate to change to brown. Tartrate ion has no effect on the test.

On spot paper, a "violet-red" spot develops rapidly with X. On a spot plate, a "red shade two" spot forms immediately, and a precipitate of the same color separates. This test resembles that for mercury, but palladium can be distinguished from mercury by the fact that the color reactions, in the case of palladium, are unaffected by treatment with hydrochloric acid.

A "yellow-orange shade one" spot forms immediately on a spot plate with XVI. On standing, a brown precipitate deposits. Tartrate ion masks the test somewhat by retarding the formation of a color and a precipitate.

**VANADIUM PENTOXIDE, VANADYL ION (VO<sub>2</sub><sup>+</sup>), AND META-VANADATE ION (VO<sub>3</sub><sup>-</sup>).** With II, a distinctive "orange-yellow shade one" ring forms on spot paper around a faded stain. If hydrochloric acid is added to the test, a "red-orange" ring forms around a pale "red-violet" stain. On standing, the stain itself becomes grayish and the ring begins to fade into the spot. On

a spot plate, a distinctive brownish gray precipitate deposits almost immediately. Tartrate ion has no effect on the test; chloride ion has only a very slight effect.

On spot paper, a very brilliant and characteristic "yellow-green tint one" spot forms with XVI. On a spot plate, a distinctive, rather intensive "yellow shade one" spot forms immediately. In either test, the presence of halogen has no effect.

## Summary

In practically all cases, the presence of chloride ion in the test solution obscures the results. In certain cases, particularly with dichromate, cobalt, and nickel, hydrochloric acid enhances the results when added to the dye spot after the test solution. There are a few cases, particularly with palladium

and mercury, where the behavior of the test on treatment with hydrochloric acid serves as the only means of distinguishing between the metals. Tartrate ion, contrary to the literature, seems in most cases to have no effect on the test.

It has been claimed that these azo derivatives of 8-hydroxyquinoline give, except in a few minor cases, consistent reactions which are specific for mercury, copper, palladium, nickel, and molybdenum as MoOCl<sub>5</sub> -- ion. The results of this research do not bear out this statement. On both spot plate and spot paper tests, mercury and palladium give color reactions with practically all the dyes studied, but only a few tests are sufficiently characteristic and intense to be considered specific. On a spot paper test, copper and nickel show a few color reactions of doubtful value, while on a spot plate no tests are observed. In either test, molybdenum gives only a few color reactions of no possible value in analytical work.

In view of this present research, it seems that the statement that polar groupings para to the point of coupling in the aromatic nucleus cause a more positive reaction should be modified so as to include only those groupings, such as hydroxyl, amino, sulfo, and carboxyl, which tend to increase the solubility of a compound in a semipolar or polar solvent such as alcohol or water. The results of this investigation are not entirely in accord with the fifth conclusion of Gutzeit and Monnier as stated above.

Condensed structures, when attached to 8-hydroxyquinoline through an azo linkage as with XIV, XV, XVI, XVII, and XVIII, tend to decrease the usefulness of the dye as an analytical reagent even though such naphthyl and biphenyl structures do contain substituents such as hydroxyl, sulfo, or amino groups which tend to increase solubility. The last two dyes mentioned are so insoluble in alcohol that there is not a sufficient concentration of active grouping (8-hydroxyquinoline) to give a positive test even with metals most likely to react.

Some new tests have been developed which may serve in the identification of metals. One reagent (XVI) has been developed for vanadium; six (II, VII, VIII, X, XII, and XV), for mercury; and six (I, II, VI, VII, X, and XVI), for palladium.

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# Determination of Carbon and Hydrogen

## On Micro- or Semimicrosamples with One Compact and Movable Apparatus

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RECENTLY (1) the authors described a movable and easily constructed apparatus for the determination of carbon and hydrogen, designed to analyze a 70-mg. sample. This apparatus has now been successfully scaled down for application to microsamples.

The apparatus in its present form (Figures 1 and 2) takes up a maximum of 57.5 cm. (23 inches) of desk space when the absorption tubes are not attached. It can be used for samples of from 2.5 to 35 mg. without increasing the combustion time appreciably beyond that for the standard combustion of microsamples. With larger samples, the combustion time is increased beyond a reasonable amount. When a microbalance is available microsamples (3 to 6 mg.) are weighed for analysis; otherwise, a 20- to 30-mg. sample is weighed using an analytical balance (weighing to 0.1 mg.) or a semimicrobalance (weighing to 0.01 mg.) for greater accuracy. The time of combustion for a microsample is usually 40 minutes; for a semimicrosample, 55 minutes. A copper oxide spiral is not necessary behind the boat for samples of either size.

Although the outfit was designed for microanalysis, with some minor alterations it could be used for samples ranging up to 35 mg., permitting the use of an ordinary analytical balance without losing efficiency as a microcombustion outfit. The apparatus is now mounted on a metal frame cast from aluminum with an iron base.

### Apparatus

Figure 2 illustrates the present setup of the apparatus, its dimensions, and the filling of the tube. The following improvements may be noted:

1. The capacity of the bulb in the gasometer has been increased to 2 liters. A gasometer of this size can deliver about 650 cc. of oxygen when the gage reads 25 cm. of mercury. Less frequent fillings of the gasometer are necessary, and the bubble rate remains constant throughout the combustion.

2. Lead chromate has been eliminated from the preheater. Its presence is unnecessary and is objectionable in that it shortens the life of the Pyrex tube. The heating coil is now in parallel with the main heating coil, making temperature control easier. The preheater coil is prepared by winding nine turns of No. 28

wire to the inch for a space of 12.5 cm. (5 inches) to give a temperature of 550° C.

3. The bubble counter has been redesigned and placed behind the scrubber. This makes hydrogen results more constant.

4. Indicating Drierite, instead of calcium chloride, has been found to have advantages in the scrubber. The internal diameter of the scrubber has been reduced to 9 mm.

5. A combustion tube 9 mm. in internal diameter and of hard combustion tubing is convenient for analyzing any sample of from 2.5 to 35 mg. If the apparatus is to be used exclusively, for microanalysis, standard tubing 6 to 7 mm. in internal diameter may be substituted. In numerous tests, the use of the narrower tubing has shown no apparent advantage.

6. The method of obtaining a differential in temperature between the end and main part of the heating unit has been changed. Previously, the turns were wound at greater intervals at the cooler end. This same result may be attained more readily by changing the gage of the wire at the cooler end and winding as for the main part of the tube. The total length of the heating coil is 32.5 cm. (13 inches). For the first 23.75 cm. (9.5 inches) No. 26 (B. & S. gage) Nichrome wire is wound. The turns are spaced at 0.6-cm. (0.25-inch) intervals except for the very beginning where, in order to compensate for end cooling, four turns are taken in the first 1.25 cm. (0.5 inch). The end is then spliced to No. 20 wire and the winding is continued for the last 8.75 cm. (3.5 inches). To allow for conduction from the hotter part of the coil, it was found necessary to take only one turn of the No. 20 wire for the first 1.25 cm. (1 inch). The turns for the remaining 6.25 cm. (2.5 inches) are taken at 0.6-cm. (0.25-inch) intervals except for the very end. To allow for the end cooling effect, three turns were taken for the last 0.94 cm. (0.375 inch).

A simple calculation will indicate why these diameters were chosen. With constant current, the heat developed in a wire is proportional to its resistance and the resistance is inversely proportional to the square of the radii of the wires employed, if the winding is evenly spaced around the same tube. No. 26 wire at 0.6-cm. (0.25-inch) intervals was found to be suitable for the first 25 cm. (10 inches) (675° to 700° C.). For the next 7.5 cm. (3 inches) a temperature of about 200° C. had to be maintained. Since the same materials (constant specific heat and rate of radiation) were used throughout the combustion coil, it was safe to assume that the heat developed was proportional to the temperature and hence the following proportion was set up:

$$\frac{(\text{Radius of No. 26 wire})^2}{(\text{Radius of desired wire})^2} = \frac{(0.00797 \text{ inch})^2}{(X \text{ inch})^2} = \frac{200^\circ \text{ C.}}{675^\circ \text{ C.}}$$

On solving for the unknown one obtains 0.0164 cm. (0.0164 inch), which is closest to the radius of No. 20 wire. That the

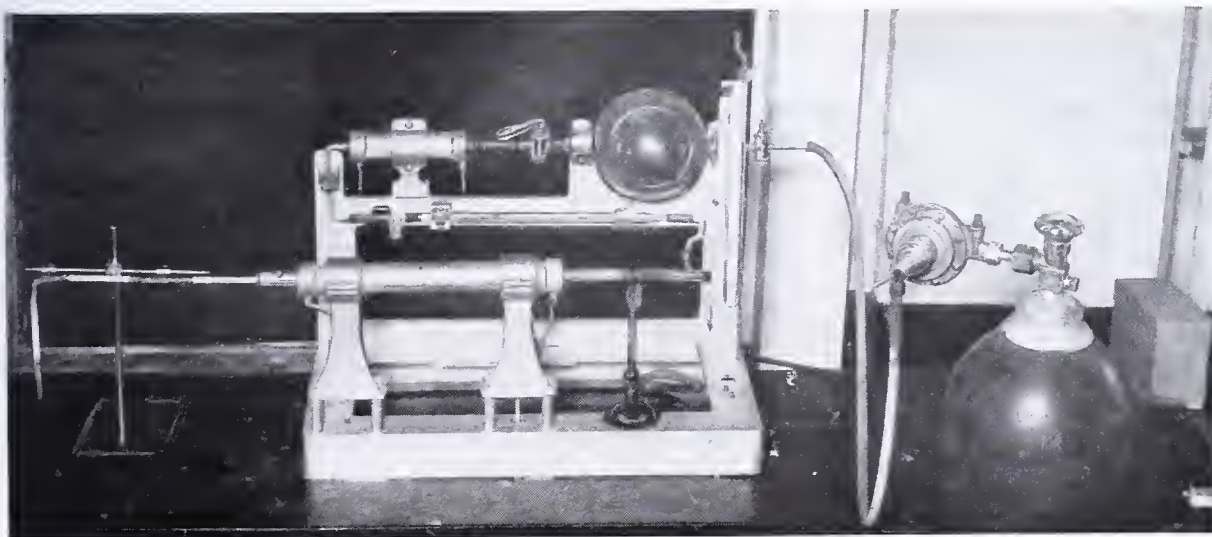


FIGURE 1. APPARATUS SETUP FOR MICROANALYSIS



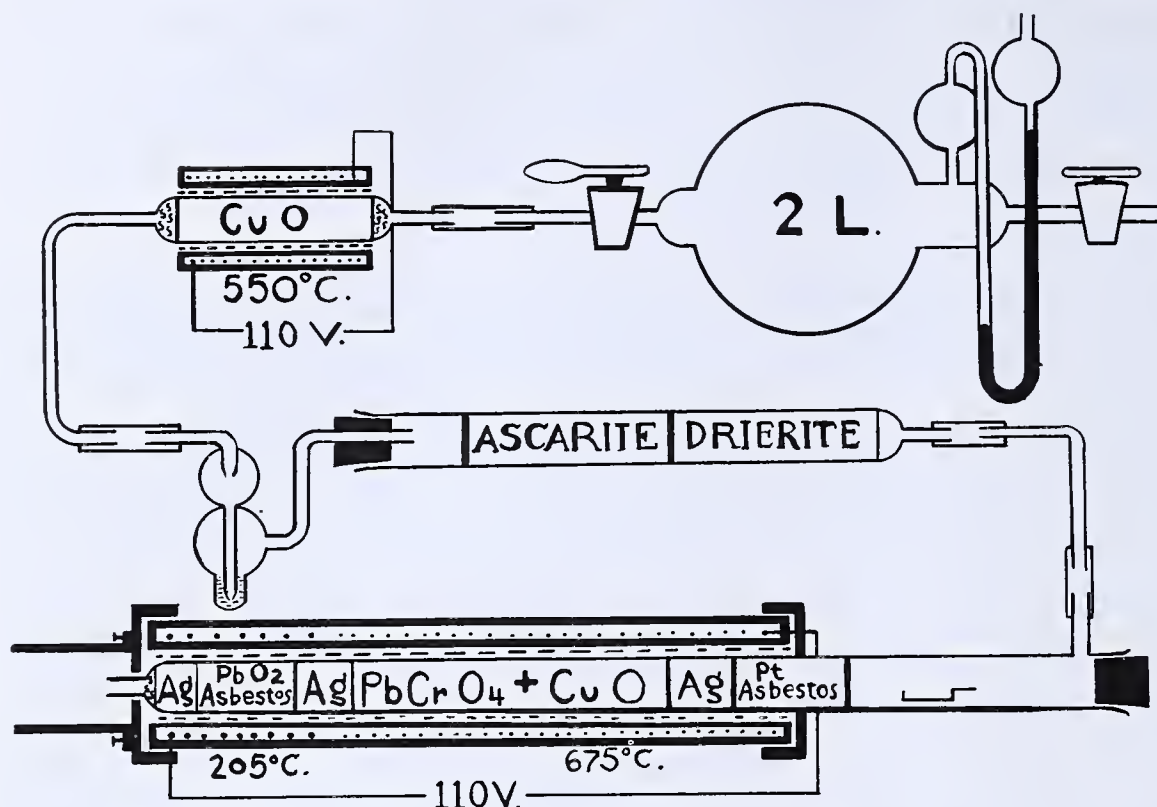


FIGURE 2. SCHEMATIC DIAGRAM OF COMBUSTION APPARATUS

reasoning is correct was evidenced by the fact that No. 20 wire for the last 6.25 cm. (2.5 inches) gave the required temperature ( $200^{\circ}\text{C}.$ ) within  $10^{\circ}$  when spaced at the same interval 0.6 cm. (0.25 inch) as the No. 26 wire. A smoothly uniform temperature is thus readily obtainable in both parts of the tube. To improve its appearance, the insulation around the heating coils is now cast in a split metal mold.

7. In order to avoid the condensation of moisture at the mouth of the combustion tube, a split metal tube hinged on one side is attached to the heating coil. When attaching the absorption tubes, the upper part of this metal tube is moved back on its hinges and replaced after connection has been made. This split tube, kept warm by conduction from the heating coil, is long enough to force the water directly into the absorption tube. An auxiliary metal tube, cut from a cork borer of the proper dimensions, may be used by sliding part of it in and out of the split tube if any additional length is needed.

The connection between the combustion and absorption tubes is made by means of the usual heavy red nitrometer tubing, previously heated to  $110^{\circ}\text{C}.$  and carefully cleaned inside and out. After more than 6 months' continuous use, no apparent deterioration had taken place. During the combustion, this

tubing is subjected to temperatures just below the boiling point of water.

8. The combustion tube is now filled as shown in Figure 2. All the asbestos plugs need not be wider than 1 to 2 mm. Precipitated silver may be used rather than the usual silver wire. It was observed that compounds with a high percentage of chlorine (more than 40 per cent) consistently gave slightly high results for carbon when silver wool, wire, or foil was used. The silver filling as used in this tube absorbed 300 mg. of chlorine (calculated from the weights and percentage of chlorine of the compounds used) before any indication of breakdown was observable. The silver could then be regenerated in the usual way. For the usual run of analyses silver wire may serve as well.

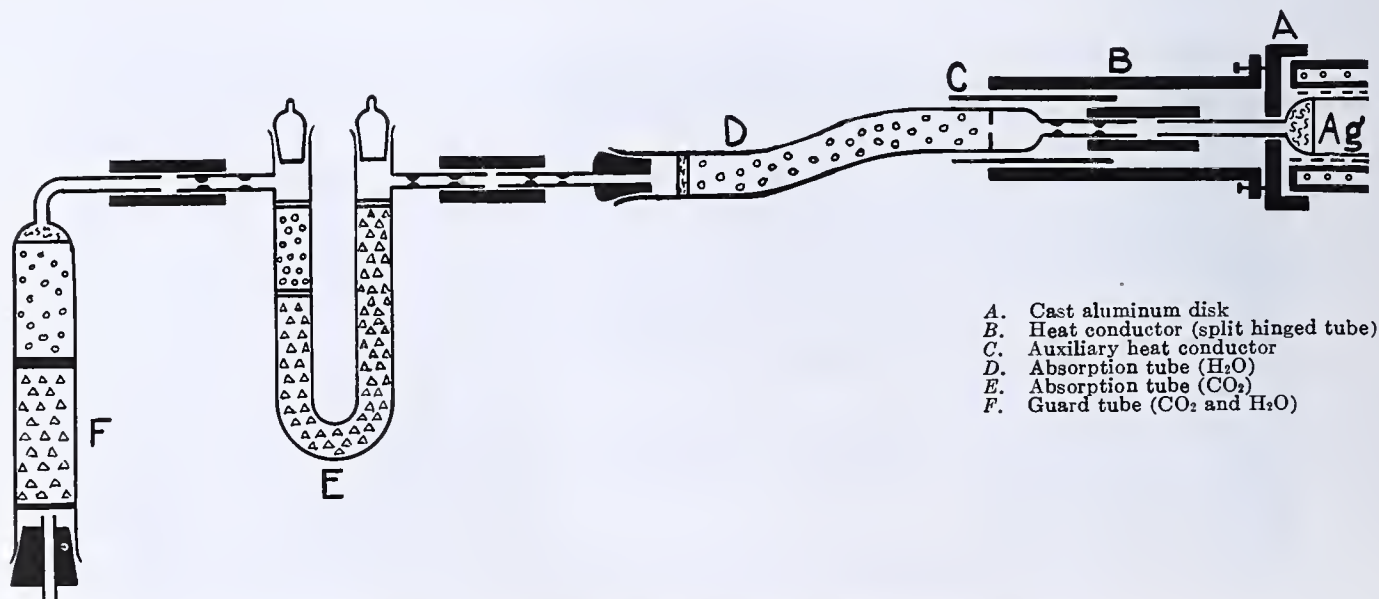
The precipitated silver may be prepared by treating silver nitrate with zinc dust (less than theoretical) and heating on a water bath. The precipitated silver is filtered off, boiled with dilute sulfuric acid to remove traces of zinc, filtered, washed, and dried in an oven. The finely divided silver is then heated at  $675^{\circ}\text{C}.$  (in the combustion train) for 1 hour, in order to avoid any shrinkage which may occur in the tube later. It is then allowed to cool and transferred to a bottle for further use.

9. For analysis of semimicrosamples, absorption tubes patterned after the usual microabsorption tubes were used (Figure 3). For microdeterminations, tubes of standard size were used.

10. The design of the support for both micro- and semimicro-absorption tubes on one small ring stand is worthy of note (Figure 1).

### Procedure and Results

For the combustion of the microsamples the standard procedure is used, 10 minutes for the first combustion and 10 minutes for reheating in order to assure complete combustion. The washing time is approximately 20 minutes, making the complete combustion time about 40 minutes. On samples of about 25 mg. the two combustion times combined

FIGURE 3. ABSORPTION TUBES FOR SEMIMICROSAMPLES  
Designed for weighing on balance pans



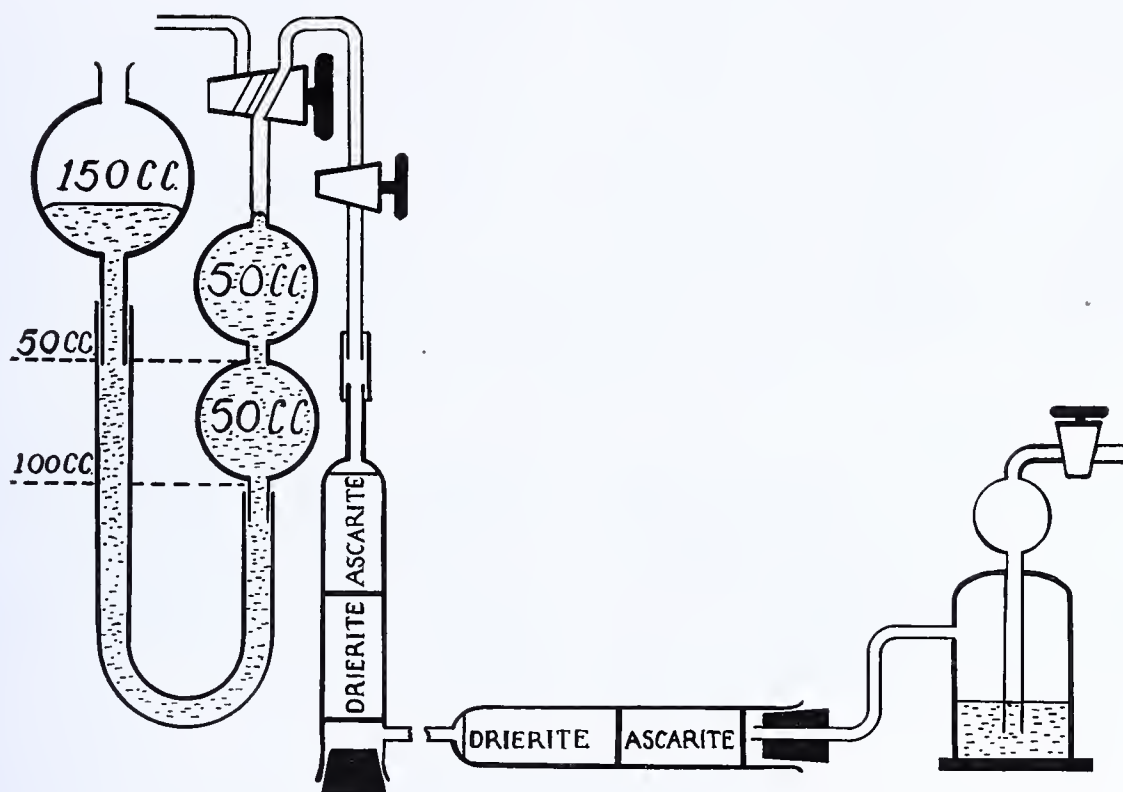


FIGURE 4. DESIGN OF ASPIRATOR FOR CONDITIONING ABSORPTION TUBES

are about 30 minutes and the washing time is about 25 minutes, making a complete combustion time of about 55 minutes.

In the combustion of the microsample 175 cc. of oxygen are used, and 325 cc. of oxygen are used for the combustion of the semimicrosample. In the case of the semimicrosample the oxygen has to be passed at the relatively rapid rate of about 5.5 cc. per minute. This can easily be achieved because the resistance of the semimicrotubes is much less than that of the microtubes. In the authors' apparatus the bubble rate was maintained at about 40 bubbles per minute. When the microtubes were attached the rate was maintained at about 4 cc. per minute or a little less than 2 bubbles per second.

The bubble rate is set at the start of the combustion. The position of the adjusting stopcock is not changed until the combustion is finished, even though at times it may vary temporarily when burned gases gather in the tube. Where combustion is difficult—i. e., with samples of high chlorine or sulfur content—the bubble rate must be slower and the time of combustion longer.

For best results (2) it is good practice, before and after the combustion, to aspirate air (dried and free of carbon dioxide) through the absorption tubes, in order to weigh the tubes filled with air rather than oxygen. For this purpose many experimenters have used the Mariotte bottle. The authors have designed an apparatus which avoids some of the disadvantages of the Mariotte bottle—the need to be present when the required amount of water has gone into the graduated cylinder, the inconvenience encountered in the refilling of the bottle, and the change in bubble rate and hence in time for the required 50 cc. as the level is lowered in the bottle. The apparatus recommended is automatic, drawing through the required amount and stopping of its own accord. There is no pouring of water and the time to deliver the required volume is always the same. A glance at Figure 4 will indicate the design.

When the reservoir, A, is lowered to the required level, the amount of air desired will be drawn through and movement will cease. The two-way stopcock may then be turned so that when

the reservoir is raised, the aspirated air is expelled. The stopcock is then returned to its original position and the apparatus is ready for use again. Instead of the 50-cc. bulbs, a 100-cc. graduated cylinder tube may be used. The bubble rate is regulated by means of a glass stopper, pinchclamp, or capillary located behind the aspirator. One filling of the tube as shown or the graduated cylinder will aspirate two sets of microtubes or one set of semimicrotubes. For microdeterminations, 50 cc. of air are passed through in 10 minutes. The tubes may then be placed directly on the balance and weighed without further delay. For the semimicrotubes 100 cc. of air are passed through in the same time (10 minutes) and the tubes are weighed directly. Both semimicro- and microtubes should be wiped carefully before weighing.

With two sets of tubes about six determinations of either micro- or semimicrosamples may be readily performed in one day. Table I shows representative results obtained on the same outfit by alternating from micro- to semimicrosamples of compounds with a variety of characteristics. A Kuhlman microbalance was used for the microsamples. The semimicrosamples were weighed to 0.1 mg. by means of an analytical balance fitted with a magnetic damper. It is apparent that for the semimicrosamples the accuracy of the results is limited by the accuracy of the weighing.

### Discussion

It is apparent that with minor differences the procedure and time are almost the same for micro- and larger samples using this apparatus. In the authors' experience both sizes of sample have given consistent results. The choice therefore depends upon the amount of material available and whether one is to use the micro- or semimicrobalance. For instructional purposes this apparatus has the advantage that one may learn the technic of analysis on semimicrosamples with the aid of an ordinary balance and then transfer the same procedure to the determination of microsamples; the only new procedure to be learned is the operation of a microbalance.

The apparatus retains the advantages of being compact and movable. It may be stored without dismantling and may be set in operation on little notice.



TABLE I. REPRESENTATIVE RESULTS

Substance	Formula	Sample Mg.	CO <sub>2</sub> Found Mg.	H <sub>2</sub> O Found Mg.	C Found %	H Found %	C Calcd. %	H Calcd. %
Resorcinol	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	5.040	12.112	2.497	65.54	5.54	65.43	5.49
		20.2	48.5	10.0	65.48	5.55	...	...
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	2.938	7.446	1.249	69.12	4.76	68.85	4.91
		19.0	48.1	8.7	69.04	5.12	...	...
<i>p</i> -Nitrobenzoyl chloride	C <sub>7</sub> H <sub>4</sub> O <sub>2</sub> NCI	3.171	5.272	0.548	45.35	1.93	45.28	2.16
		38.1 <sup>a</sup>	63.6	6.6	45.52	1.94	...	...
Cystine	C <sub>6</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> S <sub>2</sub>	3.801	4.176	1.845	29.97	5.43	30.00	5.00
		23.5	25.8	10.8	29.94	5.14	...	...

<sup>a</sup> As a safeguard 15 minutes' extra combustion time was allowed for this larger sample.

### Summary

A compact and movable outfit is described for the determination of carbon and hydrogen on samples ranging from 2.5 to 35 mg. An analytical or microbalance may be used, depending upon the amount of material that is available.

Little more time is required for the determination of the semimicrosample than for the microsample.

An aspirator is described for conditioning the absorption tubes.

Precipitated silver is used in the combustion tube to hold back large amounts of halogen.

### Acknowledgment

The authors are indebted to Mr. Weiskopf of the Empire Laboratory Supply Co., 559 West 132nd St., New York, N. Y., for his continued coöperation in the development of this apparatus, to A. Elek of the Rockefeller Institute for reviewing the manuscript, and to B. Kramer of the Jewish Hospital for his support.

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The literature in this field is so voluminous that it has been decided to refer only to two textbooks and to the authors' previous paper on the subject.

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# Determination of Iodine in Biological Materials

## Refinements of the Chromium Trioxide Oxidation Method

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QUANTITATIVE studies of iodine metabolism require adequate analytical procedures, adapted to the determination of the minute amounts of iodine present in biological materials. Owing to the complexity of former methods (10), difficulties have been experienced in obtaining consistent results, while comparative studies from different laboratories have shown considerable variation (2).

Most procedures for destroying the organic matter, preparatory to actual extraction and determination of the iodine, have involved combustion in a closed system or basic ashing. A procedure developed by Leipert (8) in 1933, however, involved oxidizing the organic matter, and all the contained iodine to iodine pentoxide, by means of chromium trioxide in a sulfuric acid medium and in the presence of ceric sulfate as a catalyst. Leipert's method also employed steam distillation in partial vacuum to separate the small amounts of iodine from the sulfuric acid solution, after the iodine pentoxide and excess chromium trioxide had been reduced by arsenious oxide.

Trevorrow and Fashena (12) employed potassium dichromate instead of chromium trioxide as the oxidizing agent, since chromium trioxide usually contains iodine and is difficult to purify. They also found that the use of arsenious oxide resulted in unwarranted high iodine values, and consequently substituted phosphorous acid in its place as the reducing agent. Later (3), moreover, they found that their former method was not quantitative and replaced the vacuum-steam distillation by a combination of aeration and distillation.

The authors have devised a simple method for preparing

chromium trioxide of low iodine content. Ceric sulfate as a catalyst may be omitted in analyses of blood, urine, feces, thyroid gland, and milk of lower iodine content than approximately 1 mg.

The chromium trioxide method is not directly applicable to biological specimens which contain very minute concentrations of iodine. Thus, for the accurate analysis of mixed dried food, combustion in oxygen by the von Kolnitz and Remington modification (7) of the Karns procedure (5) precedes chromium trioxide oxidation (9). This makes convenient the oxidation of several hundred grams of material which is subsequently completed in the chromium trioxide procedure.

Iodine may be separated from the chromic sulfate and sulfuric acid solution by a simple distillation procedure. [C. D. Stevens of the DeCoursey Clinic of Cincinnati visited the authors' laboratory to investigate their procedures for the microdetermination of iodine. He later published a procedure employing the simple distillation (11).] The apparatus, designed for making this distillation (Figure 1), is easier to manipulate and more compact than either that of Leipert or of Fashena and Trevorrow.

Phosphorous acid is most effective as a reducing agent in the quantitative recovery by simple distillation of the smaller "biological" amounts of iodine. Larger amounts (2 mg. in 100 ml. of sulfuric acid) are only 90 to 95 per cent recovered when this reagent is employed (9). The use of oxalic acid (1) may result in the distillation of reducing substances.

A permanganate procedure, proposed by Groak (4) to



prepare iodate from iodide, involves oxidation in a basic solution, reduction by nitrous acid of the excess permanganate, and subsequent reduction of the excess nitrous acid with urea. Although it is more difficult to apply than either the bromine or chlorine procedures, it has been found to be more accurate (9).

Further investigation of the starch-iodine reaction (9) indicates that reagents, presumed to be iodine-free as determined by this principle, may contain varying amounts less than that detectable. Moreover, a part of this undetected iodine is actually recovered during determinations and thus may increase the results to the extent of 0.04 to 0.05 microgram of iodate iodine per ml. of titration solution. Since starch-iodine shows this property, correction of 0.06 microgram per ml. of titration solution (3), for the amount of iodine necessary to produce color, would only increase this error.

### Apparatus

**DISTILLATION APPARATUS.** This is presented in Figure 1. (It may be obtained from the Leonard Glass Works, 1432 Minnesota Ave., Columbus, Ohio.) The digestion and distillation flask, I-a, may be of any size from 300 to 1200 ml. I-c is a standard joint of 30 mm. The coil condenser, I-g, has a dew-collecting cup, I-h, attached. Tubes having the following respective inside and outside diameters are recommended for the various pieces: I-b, 3 and 9 mm.; I-d, 3 and 6 mm.; I-f, 11 and 15 mm.; and II-d, 13 and 15 mm.

The apparatus may be mounted on one stand. It is washed by drawing water through the condenser into a flask with a stopper fitted for the joint.

II presents the entrainment trap, designed for this distillation. Its efficiency has been tested and has been found to compare well with that of other entrainment traps with larger or more intricate construction. Vapors on leaving the flask enter at II-a, follow the concentric tube around tube II-d, and enter tube II-d through opening II-c. The concentric tube is closed off at II-b, between II-a and II-c. Three small holes, 0.2 mm. in diameter, are located at II-e, the bottom of II-d, in order to permit condensed liquid to flow back into the flask. The concentric tube should have an inside cross-section area of approximately 30 sq. mm.

In III is shown a most useful type of antibump, which is easily made by first sealing a 3-mm. glass rod onto a glass tube of 3-mm. inside diameter and then cutting the tube 5 mm. from the closure and the rod at whatever length is suitable.

**BURET.** A buret of the Koch type (6), capable of measuring amounts up to 1 ml. and by which one may estimate 0.001 ml., is adequate. Titrations are conveniently made in front of white paper before a 125-watt light bulb.

### Reagents

It is usually necessary to purify those reagents which are used in large amounts. Solutions should be used because of possible heterogeneity of solids with respect to significant minute amounts of iodine.

The reagents used in the analysis of 25 ml. of blood should contain less than 0.16 microgram of iodine. The nondetectable iodine (starch-iodine reaction) is determined by difference in titrating a known barely detectable amount of iodine, added at the titration. Reagents 6 to 12, inclusive, should contain a nondetectable amount of iodine when analyzed in quantities 5 to 10 times those used in the analysis of blood.

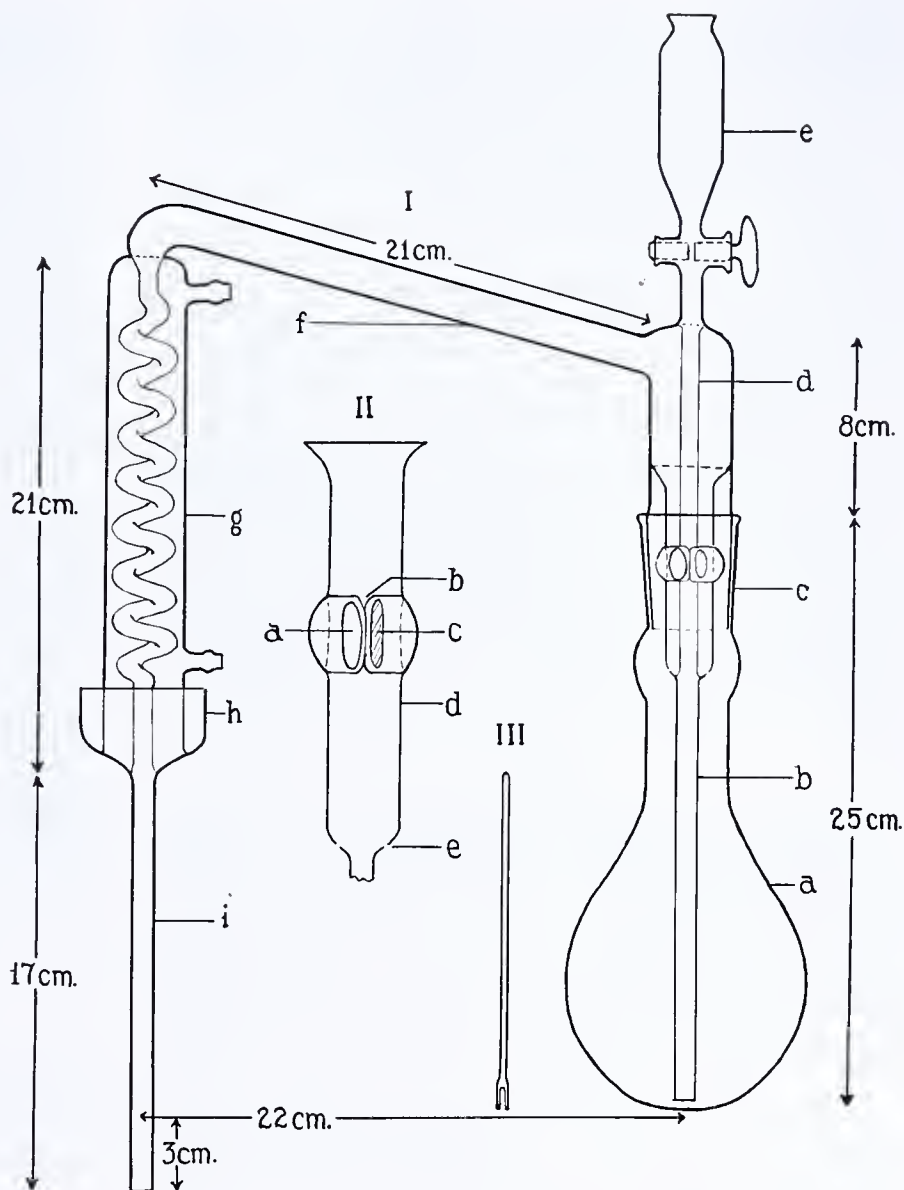


FIGURE 1. DISTILLATION APPARATUS

1. **DOUBLE-DISTILLED WATER.** Satisfactory water may be prepared by redistilling, in an all-glass apparatus, ordinary distilled water containing approximately 1 per cent of potassium hydroxide.

2. **CONCENTRATED SULFURIC ACID.** C. P. sulfuric acid usually contains only traces of iodine. By mixing 10 ml. of concentrated hydrochloric acid with 1 liter of technical sulfuric acid and boiling slowly for 30 minutes, one can prepare this grade of acid satisfactory for analysis.

3. **10 M CHROMIUM TRIOXIDE SOLUTION.** Place 1 mole of recrystallized potassium dichromate of low iodine content in the form of large crystals in a weighed 1-liter flask. Heat the potassium dichromate and 3.3 moles of sulfuric acid separately to 160° C. in an oven. Then pour the sulfuric acid into the potassium dichromate as nearly instantaneously as possible. The reaction quickly becomes violent and the chromium trioxide formed liquefies. Stir slowly until the mixture cools to 175° C. Then pour off the sulfuric acid solution and wash the solid chromium trioxide with 0.5 mole of 65 per cent sulfuric acid. The yield is from 80 to 90 per cent. Add 0.6 ml. of water for each gram of chromium trioxide.

4. **5 M PHOSPHOROUS ACID SOLUTION.** Each milliliter of solution should contain 0.41 gram of anhydrous phosphorous acid. The authors have prepared phosphorous acid of required quality by adding 1 part of phosphorous trichloride in small amounts to 1.5 parts of continuously cooled water. After the reaction is complete, water and hydrogen chloride are removed by boiling, first to 150° C. under atmospheric pressure, and then to 180° C. under reduced pressure.

5. **5 M POTASSIUM CARBONATE SOLUTION (0.69 gram per ml.).** It may be necessary to subtract a small blank for this reagent, used in the analysis of urine.

6. **0.5 M POTASSIUM CARBONATE SOLUTION.**

7. **0.1 M SULFUROUS ACID SOLUTION.** Place 11 grams of



sodium bisulfite in a distilling flask and put the condenser stem of the apparatus in 1000 ml. of water. Add sufficient dilute sulfuric acid through the entry tube to decompose the sodium bisulfite and briefly distill. This solution decomposes readily.

8. 0.2 *M* POTASSIUM PERMANGANATE SOLUTION, 0.0316 gram of potassium permanganate per ml. of solution.

9. 85 PER CENT PHOSPHORIC ACID.

10. 1.5 *M* SODIUM NITRITE SOLUTION, 0.104 gram per ml. of solution.

11. 5 *M* UREA SOLUTION, 0.3 gram per ml. of solution.

12. ONE PER CENT STARCH SOLUTION. Add 10 grams of soluble starch in the form of a paste and 10 mg. of powdered mercuric iodide to 1 liter of boiling water and then boil the solution 5 minutes.

13. 0.30 *M* POTASSIUM IODIDE SOLUTION, 0.0498 gram of potassium iodide per ml. of solution. This solution should give no color with starch when cooled to 0° C.

14. 0.0002, 0.001, AND 0.01 *N* SODIUM THIOSULFATE SOLUTIONS. Dilutions are made of 0.1 *N* sodium thiosulfate (24.82 grams of the hydrated salt per liter), and 0.5 ml. of concentrated ammonium hydroxide is added per liter as a preservative. Solutions should be kept in a dark and cool place and standardized each week against standard dilutions of 0.1 *N* potassium biniodate (32.51 grams per liter). If the solution employed in the standardization of the 0.0002 *N* thiosulfate is approximately 2 ml. in volume; 1 *M* in sodium chloride; 0.2 *M* in phosphoric acid, and 0.005 *M* in potassium iodide; and if 0.2 microequivalent of iodate is titrated, then the error of standardization will be small.

## Procedure

**OXIDATION.** The procedure as given below is for amounts of biological materials of normal iodine content, as determined for this region. The biological specimen, which should be in a homogeneous state, is mixed in a distillation flask with an amount of chromium trioxide solution which provides chromium trioxide in excess of the amount required for complete oxidation. Since the reaction is vigorous, the sulfuric acid must be added in small portions at first and the specimen must be cooled or permitted to stand between additions.

**BLOOD.** To 25 ml. of blood in a 1200-ml. flask add 38 ml. of chromium trioxide solution. Then add 15 ml. of sulfuric acid slowly while the flask is being rotated. After the mixture no longer boils vigorously, repeat the operation. Finally add 160 ml. of sulfuric acid.

**URINE.** Add 1 ml. of 5 *M* potassium carbonate solution to 100 ml. of normal urine. Place 2 antibumps in the flask and concentrate the urine to 10 ml. In order to avoid loss by foaming evaporate slowly, or boil in the presence of a jet of compressed air. Add 10 ml. of chromium trioxide solution and 50 ml. of sulfuric acid.

**DRIED FOOD.** Dried food (or other specimens of low iodine content) containing at least 2 micrograms of iodine is oxidized according to the procedure of von Kolnitz and Remington (7). The basic absorbing solution and washings are boiled down to 10 ml. and treated with 10 ml. of chromium trioxide solution and 50 ml. of sulfuric acid.

In the analysis of 5 grams of dried and powdered feces, 0.1 to 0.2 gram of dried and powdered thyroid, or 25 ml. of milk, 30, 5, and 30 ml. of chromium trioxide solution are used, respectively. In general, 5 ml. of sulfuric acid are employed for each milliliter of the 10 *M* chromium trioxide solution; however, a minimum of 50 ml. of sulfuric acid is used.

After the addition of the sulfuric acid the mixture is heated rapidly in a hood to 220° C. and maintained at that temperature for 5 minutes. This heating suffices to decompose the excess chromium trioxide to a concentration smaller than 30 milliequivalents per 100 ml. of sulfuric acid.

**DISTILLATION.** When the flask has cooled to below 100° C., a volume of water equivalent to 25 ml. in excess of the sulfuric acid employed is added. Two antibumps are then added and the mixture is stirred thoroughly by rotating at a 45° angle. The flask is then connected to the apparatus, which has been first thoroughly washed. An Erlenmeyer flask containing an antibump, 0.5 ml. of 0.5 *M* potassium carbonate, and 0.5 ml. of 0.1 *M* sulfurous acid is placed under the condenser stem so that the tip dips into the solution. The flask is then heated and as soon as the distillation begins, 5 ml. of 5 *M* phosphorous acid are added through the entry tube for each 100 ml. of sulfuric acid in the flask. The distillation is made at approximately the rate of 100 ml. per 15 or 20 minutes. A volume equivalent to 25 ml.

plus one-half the volume of acid, but a maximum of 100 ml., is distilled. This procedure has been tested for amounts of sulfuric acid from 50 to 400 ml. The distillate is boiled down to from 3 to 5 ml. The samples are then quantitatively transferred to 25-ml. Erlenmeyer flasks, and boiled to a 1-ml. volume.

**PERMANGANATE OXIDATION.** Place the sample in a shallow boiling water bath. Add 0.2 *M* potassium permanganate, from the pipet of a dropping bottle, directly into the solution until a permanent purple coloration results. One drop (0.03 ml.), or two, is usually sufficient. After adding the permanganate, rotate the solution gently upon the sides of the flask and heat the samples for 2 minutes. Then add 2 drops (0.06 ml.) of 85 per cent phosphoric acid. No decolorization of the permanganate should occur. After 2 minutes add 1.5 *M* sodium nitrite solution drop by drop directly until all manganese dioxide and excess permanganate are reduced. Add 1 drop of nitrite solution in excess and thoroughly rotate the solution upon the sides of the flask, in order to reduce any manganese dioxide particles there. Finally, after the solution has stood for 2 minutes, add 1 drop of 5 *M* urea. Rotate the solution thoroughly upon the walls of the flask, and permit the sample to stand 4 minutes longer in the water bath. Cool the sample to room temperature (20° to 30° C.) before titration.

**THE TITRATION.** One drop (0.03 ml.) of 0.3 *M* potassium iodide is added to the samples. One drop of starch solution is then added and the liberated iodine is titrated with 0.0002 *N* or 0.001 *N* thiosulfate solution.

The distillation, permanganate oxidation, and titration procedures which have been described should be slightly modified for specimens containing more than 20 micrograms of iodine. The distillate should be collected in 2 ml. each of 0.5 *M* potassium carbonate and 0.1 *M* sulfurous acid. The permanganate oxidation should be made in a 5-ml. volume with appropriately larger quantities of reagents. At the titration as much as 1 ml. of potassium iodide solution may be added. The starch solution should be added just before the end point.

TABLE I. DETERMINATION OF IODINE IN BIOLOGICAL SUBSTANCES

Specimen	Iodine Content	Iodine Added as Iodo-phen	Iodine Recovered	%
		Micrograms		
Reagents for 25 ml. of blood	0.06	...	....	...
	0.05	...	....	...
25 ml. of blood	0.50	1	1.49	96.0
	0.52	1	1.51	98.0
	0.53	20	20.3	99.0
	0.56	20	20.4	99.0
	0.53	400	399.0	99.6
		400	402.0	100.4
0.1 gram of thyroid	63.8	...	....	...
	64.7	...	....	...
0.2 gram of thyroid	129.8	...	....	...
	131.2	...	....	...
25 ml. of milk	3.58	20	23.3	98
	3.66	20	23.4	99
	3.62			
2.5 grams of feces	22.8	...	....	...
	23.5	...	....	...
5.0 grams of feces	46.3	...	....	...
	46.8	...	....	...
100 ml. of urine	4.39	20	24.5	100.0
	4.56	20	24.7	101.0
	4.48	400	398.0	98.4
		400	400.0	98.9

Iodine factors for the standard thiosulfate solutions are as follows:

1 ml. of 0.0002 <i>N</i> thiosulfate	4.23 micrograms
1 ml. of 0.001 <i>N</i> thiosulfate	21.16 micrograms
1 ml. of 0.01 <i>N</i> thiosulfate	211.6 micrograms

## Application of the Method

The method has been tested on several types of biological specimens. To demonstrate the percentage of recovery, the determinations shown in Table I were made. Standard solutions of recrystallized iodophen (tetraiodophenolphthalein) were added to the fluid specimens.



These, as well as other results obtained, indicate that rigorous application of the method as described should make possible determinations with a precision of within 5 per cent of amounts of iodine from 2 to 400 micrograms. Below 2 micrograms the possible error of titration of from 0.02 to 0.04 microgram must be considered. This source of error, as well as others, makes impossible the limitation of error to within even 10 per cent in determining amounts of iodine below 0.5 microgram.

With four complete apparatus available, four analyses of blood have been made easily by one person in 2.5 hours.

Different investigators have employed varying methods of determining the normal iodine content of human blood (10). Considerable variation of the average values obtained, and of the range, have resulted (2). This study (9) indicates that certain of the higher ranges may be due to the use of chlorine as an oxidizing agent and to the presence of iodine in the potassium hydroxide employed. Nevertheless, employment of this chromium trioxide procedure has yielded consistently since August, 1935, human blood values in this region of around 4 micrograms per 100 ml.

### Summary

Peculiarities of the starch-iodine reaction necessitate the use of reagents of known iodine content.

Methods which have been devised permit the preparation of reagents of desirable purity with respect to small amounts of iodine.

The permanganate procedure yields results which are

more accurate than those obtained by the use of bromine or chlorine.

A distillation procedure, using a special apparatus, renders vacuum-steam distillation and aeration-distillation unnecessary.

Results obtained indicate that a precision of 5 per cent is attainable with amounts of iodine from 2 to 400 micrograms.

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# Estimation of Copper, Zinc, and Cobalt (with Nickel) in Soil Extracts

## Dithizone Methods Particularly Adapted to Examination of Soils

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THE present paper is chiefly devoted to isolation and measurement of small amounts of copper, zinc, and cobalt, such as are usually found in soils, using an elaboration of dithizone methods. The procedures are thought to be generally applicable to extraction of these metals from almost any dilute aqueous solution, and to measurement of the separated metals.

### Preliminary Work

In addition to the methods for preparing apparatus and reagents previously described (5), the following may be added:

After the glassware has been cleaned by usual methods, rinse with dilute (1 to 3) hydrofluoric acid to remove the siliceous film which sometimes adheres very firmly to glass after it has held soil or rock extract, which usually contains soluble silica. After the hydrofluoric acid rinse, wash immediately with pure water. To test for freedom from metals extractable by dithizone, place in the vessel about 50 cc. of the 0.02 N ammonia wash, described below, 5 cc. of chloroform, and a few drops of dithizone solution and shake vigorously. The chloroform should remain colorless or greenish. If it is colored, further purification is necessary.

Stopcocks are lubricated by a paste of flake graphite in glycerol. Very pure dithizone, which is necessary for precise work, may be prepared by the method of the Association of Official Agricultural Chemists (1). The procedure described by Wilkins *et al.* (13) provides a somewhat less pure dithizone.

Aqueous solutions of reagents containing objectionable metals, such as copper, zinc, and lead, may be freed of them by making slightly alkaline with ammonia, then shaking out repeatedly with dithizone in chloroform till no more metal is extracted. If dithizone in the aqueous solution is objectionable, it may be removed by shaking out repeatedly with chloroform. In nearly all cases carbon tetrachloride may be used instead of chloroform, though it seems to have more tendency to form emulsions than chloroform, and it is perhaps preferable to chloroform for extracting metals from acid solutions. Ordinary concentrated hydrochloric acid when distilled carries some zinc over with it. To purify it by distillation it should be diluted with water, so that it contains not over 20 per cent of hydrochloric acid, and distilled through all-Pyrex apparatus. Ammonia may be purified by distillation without dilution.

### Additional Procedures

Reagents and apparatus are rarely quite free of zinc; therefore it is important to make frequent blank tests which will permit a proper correction. Because the blank frequently amounts to a considerable portion of the total found and is variable in amount, the final result may have considerable plus or minus percentage errors. Perhaps this should be expected when working with the very small quantities of metals, 1 to 20 micrograms (gamma), here considered.

In extracting a solute from solution A by means of an immiscible solvent B, there is nearly always a partition of the



solute between the two solvents. In consequence of this it is necessary to extract solution A by means of solution B perhaps two to five times in succession in order to effect nearly complete separation.

A number of metals may be separated by extraction with dithizone from suitably acidified solutions. Such extractions require much more vigorous and longer continued agitation of the two liquids together than do extractions from slightly alkaline solutions. Detailed procedure for each case may readily be developed from the experience of the analyst.

Exact separations usually require washing each of the two separated liquids with a small portion of the other solvent, adding this wash to the main portion of the same solvent. Thus the chloroform extract is washed with water and the aqueous solution with chloroform. In drawing off the chloroform extract, one must decide whether to leave a little of the chloroform with the aqueous solution or run a little of the aqueous solution out with the chloroform extract. The decision must depend upon the particular separation in question.

Excess dithizone usually must be washed out of the chloroform solution of the metal dithizonates being extracted, by two or more successive washings with the 0.02 *N* ammonia wash. A series of separatory funnels containing the wash solution is to be used for the successive washings. To avoid loss of metal in these washings, it is well to use the last dithizone extract to collect any metal dithizonates from the successive wash solutions by washing each of them with it and finally adding it to the main portion of the washed extract. This requires less chloroform and collects all the extract. Considerable experience with the use of dithizone for separating or measuring small amounts of metals must be acquired before very good results should be expected.

**HANDLING OF EMULSIONS.** Persistent emulsions may be broken by filtering through a cotton plug in the neck of a small funnel, or by drawing off the clear portion of the chloroform, adding fresh chloroform to the emulsion, agitating gently, letting it separate, and again drawing off the clear portion. This is repeated if necessary to recover all of the dithizonate from the emulsion.

A similar procedure may be used to avoid long waiting for the two liquids to separate sharply, even though there is not much emulsion present. Frequently small droplets of the chloroform are slow in settling out of the aqueous phase.

**PRESERVATION OF DITHIZONE EXTRACT.** The dithizone compounds with metals are slowly decomposed by light and air; therefore they should be kept in the dark, well stoppered, until they are titrated to determine the amount of metal present. This should not be delayed more than a few hours.

### Estimation of Isolated Metals

The previous paper (5) describes various methods for estimating the amount of zinc in the chloroform dithizone extracts by color comparisons, and also gives the method for titrating the zinc dithizonate with bromine.

Recent refinements of the bromine titration procedure have made it sensitive enough for measuring all but amounts of 2 gamma or less of zinc, which are better estimated by color comparison.

**PREPARATION OF BROMINE SOLUTION.** Dissolve 1 cc. of pure bromine in 100 cc. of carbon tetrachloride for a stock solution to be preserved in a glass-stoppered bottle away from light. For the working solution dissolve 1 cc. of the stock solution in 200 cc. of carbon tetrachloride and keep in a dark bottle connected with a 2-cc. buret, so that the buret may be filled to zero automatically by suction at the top of the buret, not by pressure on the solution of bromine in carbon tetrachloride. Avoid entrance of moisture or air as much as possible into the bromine solution. Except when in use, the bromine solution should be kept in a dark glass-stoppered bottle away from light and air. This solution is not

constant in oxidizing power, slowly becoming weaker, and therefore should be checked against a known amount of zinc or other metallic dithizonate every day or two. A solution of 7.4 mg. of arsenious oxide dissolved by heating with 0.2 gram of sodium bicarbonate and diluted to 100 cc. provides a good standard for measuring the strength of the bromine solution. One cubic centimeter of the arsenious solution reduces the bromine equivalent to very nearly 5 gamma of zinc as the dithizonate. When fresh, 1 cc. of bromine solution is equivalent to 7 to 9 gamma of zinc as dithizonate. This bromine solution is nearly equal to 0.001 *N* thiosulfate.

**TITRATION.** Place the chloroform solution of zinc dithizonate to be titrated in a 60-cc. narrow-mouthed, glass-stoppered bottle, and add the bromine solution slowly with frequent shaking of the bottle until the red color fades to colorless, or yellowish when much zinc is present. If the amount of bromine required is approximately known it may all be added at once, quickly. Several minutes should be allowed for completion of the reaction. The end point is not distinct; therefore add some excess of bromine, and after 5 minutes about 1 cc. of the 20 per cent potassium iodide in water, followed by a little starch solution and 5 cc. of water containing 1 per cent sodium bicarbonate. The excess bromine liberates iodine which is titrated to colorless with 0.001 *N* thiosulfate. One per cent of sodium bicarbonate added to the boiled water used to dissolve the sodium thiosulfate keeps it from losing strength for several days. This method is applicable to amounts of zinc from 1 to 30 gamma; for smaller amounts the color comparison method is better (5). If insufficient bromine has been added, no blue will appear on adding iodide and starch. In this case, add more bromine till blue, shake a minute, then complete the titration with the thiosulfate. More reliable results are obtained if excess bromine is added before back-titration is begun.

Lindner (8) has measured the zinc in the dithizone complex by adding an excess of ceric sulfate and titrating back with ferrous sulfate, using *o*-phenanthroline ferrous complex as indicator. He reports excellent results, not yet offered for publication.

Copper, lead, cobalt, cadmium, and some other metals may be extracted by dithizone and amounts measured by titration with bromine much as zinc is estimated. In order to determine the equivalence of the bromine solution with respect to the particular metal in question, a 10-gamma portion of the metal is extracted by the appropriate dithizone procedure and titrated with the bromine solution.

### Isolation of Copper, Zinc, and Cobalt

The following procedures have been used for removal and isolation of 1 to 50 gamma of copper, zinc, and cobalt from soil extracts. (If nickel is present, an indefinite amount will be included with the cobalt.) The procedures should be equally applicable to any dilute aqueous solution which does not contain the noble metals or mercury. These extracts were made by use of a normal solution of potassium chloride containing enough acetic acid to make the pH about 3.6 with a total acidity about 0.04 *N*. The solutions contain some iron and manganese. To prevent them from interfering, 2 cc. of a 10 per cent solution of ammonium citrate are added to 400 cc. of the soil extract before beginning the separations.

If a solution contains many of the metals which form dithizonates, the isolation of any single one may be very complicated. However, in soil extracts there are likely to be only a few present in appreciable amounts, so that the difficulties are not great.

**ISOLATION OF COPPER.** Copper is removed from the acid solutions by repeated extraction with dithizone in chloroform. Bismuth, if present, will be included with the copper. The solution may have a pH of 1 to 4. After copper and bismuth have been separated from the original solution, wash the extract with 20 cc. of 0.01 *N* hydrochloric acid to remove any zinc, which is added to the main solution, then wash the copper solution free of excess dithizone by the dilute ammonia wash. Extract copper and bismuth from the chloroform by shaking with 1 per cent nitric acid. Neutralize the acid solution with sodium or potassium hydroxide, add enough tartaric acid to make the solution 0.5 *N*, and again extract the mixture with dithizone as at first.



The copper again combines with dithizone, while very little of the bismuth does.

Bismuth may be separated from copper by extracting copper with dithizone from a solution of both in 0.5 *N* hydrochloric acid. Bismuth remains in the acid aqueous solution. However, it is difficult to extract the copper completely from 0.5 *N* hydrochloric acid. Several successive extractions are necessary. These separations may not be perfect. They have not been critically examined by the writer, since no evidence of bismuth in the soils studied has been found. A somewhat different procedure has been described by Stolze (11).

The copper extract is washed free of dithizone by 0.02 *N* ammonia, then drawn off into a small bottle for estimation of copper by the bromine titration method, described above.

TABLE I. SEPARATION OF KNOWN AMOUNTS OF COPPER, COBALT, AND ZINC BY THE DITHIZONE METHOD

Expt. No.	Taken		Found			Treatments
	Cu	Co	Zn	Cu	Co	
Gamma						
42	10	..	..	10	..	3 extractions from 200 cc. of KCl solvent
43	..	10	..	..	10	1.8 5 extractions with 0.01 <i>N</i> HCL
45	..	..	10	..	..	(8.6 3 extractions with 0.01 <i>N</i> HCL
						(0.7 4th extraction with 0.01 <i>N</i> HCL
47	..	..	10	..	10	No separations
48	10	10	10	10.5	9.4	7.2 4 extractions from 300 cc. of KCl solvent
49	10	10	10	11.2	10.0	9.1 4 extractions from 300 cc. of KCl solvent
50	Blank on 200 cc. of KCl solvent			0.8	0.6	2.1 3 extractions for each
51	10	10	10	12.3	10.6	7.9 From 200 cc. of KCl solvent
52	..	10	..	1.3	10	.. From 200 cc. of KCl solvent
53	10	..	10	10.5	..	10 .....
54	..	10	..	2.6	10	1.4 Direct, no separation
55	..	..	10	1.0	1.1	10 3 extractions on each from 200 cc. of KCl solvent
						10.6 .....
57	..	..	10	..	..	..
58	10	..	..	8.7	..	.. } Simple extraction, no separations
59	..	10	..	..	10.6	.. } .....
60	..	..	10	..	..	10.0 } .....
12	50	..	10	..	..	9.8 3 extractions by 0.05 <i>N</i> HCL
13	..	50	10	..	..	10.8 3 extractions by 0.01 <i>N</i> HCL
15	10	50	..	12.1	..	.. 2 extractions by 0.05 <i>N</i> HCL
18	50	..	..	..	..	3.1 2 extractions by 0.05 <i>N</i> HCL
19	..	50	..	..	..	3.1 2 extractions by 0.05 <i>N</i> HCL
39	..	10	..	..	9.9	.. By choline test
40	..	10 nickel	..	7 nickel	..	.. By nitroaminoguanidine
41	..	30 nickel	..	26 nickel	..	.. By nitroaminoguanidine

**SEPARATION OF ZINC AND COBALT.** After removal of copper and bismuth, neutralize the aqueous solution to pH 7 to 9 (phenol red) and extract zinc and other metals which may accompany it (such as lead, cobalt, nickel, and cadmium) with dithizone and chloroform. Wash free of excess dithizone with ammonia wash. Remove the zinc, including lead and cadmium, if present, from the cobalt by shaking out three or more times successively with 20- to 30-cc. portions of 0.01 *N* hydrochloric acid. If there is much more cobalt than zinc in the solution being analyzed, the separation above described is imperfect, and some cobalt is extracted with the zinc by the 0.01 *N* hydrochloric acid. To complete the separation repeat the process once or twice, by again making the acid extract alkaline, recombining with dithizone as at first, and again extracting the zinc with 0.01 *N* hydrochloric acid. Zinc, lead, and cadmium enter the acid solution, while the cobalt and most of the nickel remain in the chloroform. Wash free of excess dithizone with ammonia wash, and draw off the cobalt solution, including nickel, for estimation of cobalt by bromine titration. (The titrated solution is brownish if much cobalt is present.)

The acid aqueous solution contains the zinc and perhaps lead and cadmium. Bring the pH to 7 to 9 again, extract the zinc with dithizone in chloroform, wash free of excess dithizone, and draw off the zinc solution for titration with bromine. Since lead and cadmium have not been encountered in the soil extracts examined, little study of a means of separating them has been made by the writer.

In case lead is present, addition of 1 per cent of potassium cyanide to the solution will prevent zinc and cadmium from combining with dithizone, so that the lead alone is extracted. The details of procedure are given by Clifford and Wichmann (2), Hubbard (6), and others (5, references).

Sandell (10) estimates zinc in mixture with lead by titrating with dithizone in presence of thiosulfate at pH 4.1. This procedure has not been examined by the writer.

Cadmium is neatly and easily separated from zinc by dithizone in 5 per cent sodium hydroxide (4, Fischer's method); the zinc remains in the alkaline aqueous solution from which it may be extracted by dithizone as usual after neutralizing the excess of sodium hydroxide. Cadmium present as dithizonate in the chloroform extract may be estimated the same as zinc, by titration with bromine as described above.

In using this scheme for separating these metals, if both copper and cobalt are present, as they usually are, the copper must be removed from the solution before it is made alkaline, because both copper and cobalt are extracted from alkaline solutions by dithizone and are not separated by shaking out with acid. But if it is desired to determine the zinc only in a mixture of the three metals, all may be extracted at once from alkaline solution. Then the zinc is removed from this extract by shaking out with 0.01 *N* hydrochloric acid as above described, leaving the copper and cobalt together in the chloroform, the acid solution containing the zinc is made alkaline, and the zinc is again extracted by dithizone as usual.

Attempts to separate nickel from cobalt by extracting the chloroform solution of the dithizonates of both with acid were not successful. Hydrochloric acid 0.01 to 0.5 *N* was used. The stronger the acid the greater was the amount of nickel and cobalt extracted, but even 4 *N* hydrochloric acid decomposed cobalt dithizonate only slowly and incompletely. Probably 0.5 *N* hydrochloric acid will extract all the nickel from such a mixture together with much of the cobalt. Then, if both are extracted by dithizone from the acid aqueous extract after it has been made alkaline, the dithizonates can be again extracted with 0.5 *N* hydrochloric acid and thus more of the nickel isolated. Repetition of this tedious procedure might effect almost complete separation of the two metals.

**SEPARATION AND ESTIMATION OF COBALT AND NICKEL.** No satisfactory means of separating these metals by dithizone has been found suitable for the small amounts present in the soil extracts examined. The color methods here described afford a partial solution of the problem.

A recent paper by Fischer (3) describes determination of numerous metals by dithizone but omits separation of nickel and cobalt.

The nitroso R salt test of Van Klooster (12) is not satisfactory, on account of lack of sensitivity and because the color of the reagent itself tends to obscure the color of its cobalt compound.

The choline test (Jacobs and Hoffman, 7) has been found specific for cobalt and not interfered with by small amounts of nickel, zinc, or copper. It may be made by adding to the neutral solution (about 2 cc.) 1 cc. of 1 per cent choline hydrochloride and 2 cc. of a 2 per cent solution of potassium ferrocyanide. Appearance of an emerald-green color indicates cobalt.

The nitroaminoguanidine test (Phillips and Williams, 9), which seems to be specific for nickel, may be made by adding to 5 to 10 cc. of the solution 0.5 cc. of the reagent (1 per cent in dilute nitric acid) and 1 to 2 cc. of *N* sodium hydroxide, or enough to make alkaline. Presence of 5 gamma of nickel in 10-cc. volume is indicated by a clear blue-green color, not interfered with by several times as much cobalt. (A cobalt chloride marked c. p. contained enough nickel to give the test distinctly in 30 gamma of cobalt.)

For lack of a better method, the following is proposed for estimating the amount of nickel and cobalt in the mixture after the dithizonates have been titrated with bromine: Empty the titrated mixture into an evaporating dish, and evaporate to dryness on the steam bath. Add hydrochloric and nitric acids and evaporate to dryness once or twice to remove organic matter. Then evaporate once with hydrochloric acid to remove nitrates and take up in a little dilute hydrochloric acid. Divide the solution and estimate cobalt in one part by the choline test (7) and nickel in the other part by the nitroaminoguanidine test (9).

This procedure is proposed for use where the amounts of the metals are 5 to 10 gamma, too little for separation by the usual chemical methods.

Results

Results obtained in separation of approximately known amounts of the metals are given in Table I.

On account of impurities in the metals used as standards and in reagents, of imperfection in separations, of smallness of the amounts of metals taken for analysis, and of large volumes of solution involved, considerable variations in amounts of metals found may be expected. However, since the amounts concerned are all stated as micrograms (1 microgram = 1 gamma = 0.001 milligram), most of the results are fairly good. Repeated trials showed that the cobalt solution



used contained about 0.6 gamma of zinc in 1 cc. which was calculated to contain 10 gamma of cobalt (experiment 19). The copper solution used in these experiments contained zinc. Estimation of the amounts in each case except 39, 40, and 41 was made by bromine titration of the dithizone extracts. The separations were made by decomposition of the dithizone extracts with dilute hydrochloric acid of various normalities as indicated in Table I. Usually 20 to 30 cc. of the acid were used for each extraction. In experiment 39 cobalt was estimated by the choline test on the dithizone extract after it had been titrated with bromine which indicated 10 gamma of cobalt.

TABLE II. COPPER, COBALT, AND ZINC  
Extracted from soils by acidified potassium chloride solvent

Soil No.	Copper P. p. m.	Cobalt P. p. m.	Zinc P. p. m.
59	1.1	0.8	7.8
64	2.1	5.3	4.3
78	1.6	4.0	4.5
89	0.5	1.2	5.3
112	0	0.4	1.2
122	0.5	0.4	2.2
136, top	1.2	2.9	5.6
136, subsoil	0	0.2	1.4
144	0	0.4	1.3

The nickel found by the nitroaminoguanidine test in experiments 40 and 41, after the dithizone extraction, is low for reasons not known. There appears to be a tendency for some cobalt and zinc to be included with copper. Quantitatively these figures are not very good, but they show the degree of accuracy that may be expected.

Since the purpose of this study was chiefly to find a means of making reliable estimations of zinc in soil extracts, no great effort was made to work out procedures capable of giving more exact results for other metals. In absence of interfering substances it seems that 10 to 30 gamma of each of these metals may be easily extracted from aqueous solutions by dithizone and estimated by titration with bromine, with an accuracy of  $\pm 10$  per cent. Where separations have

been made by repeated extractions, results are less accurate because of imperfection in methods and uncertainty of amount of the blank.

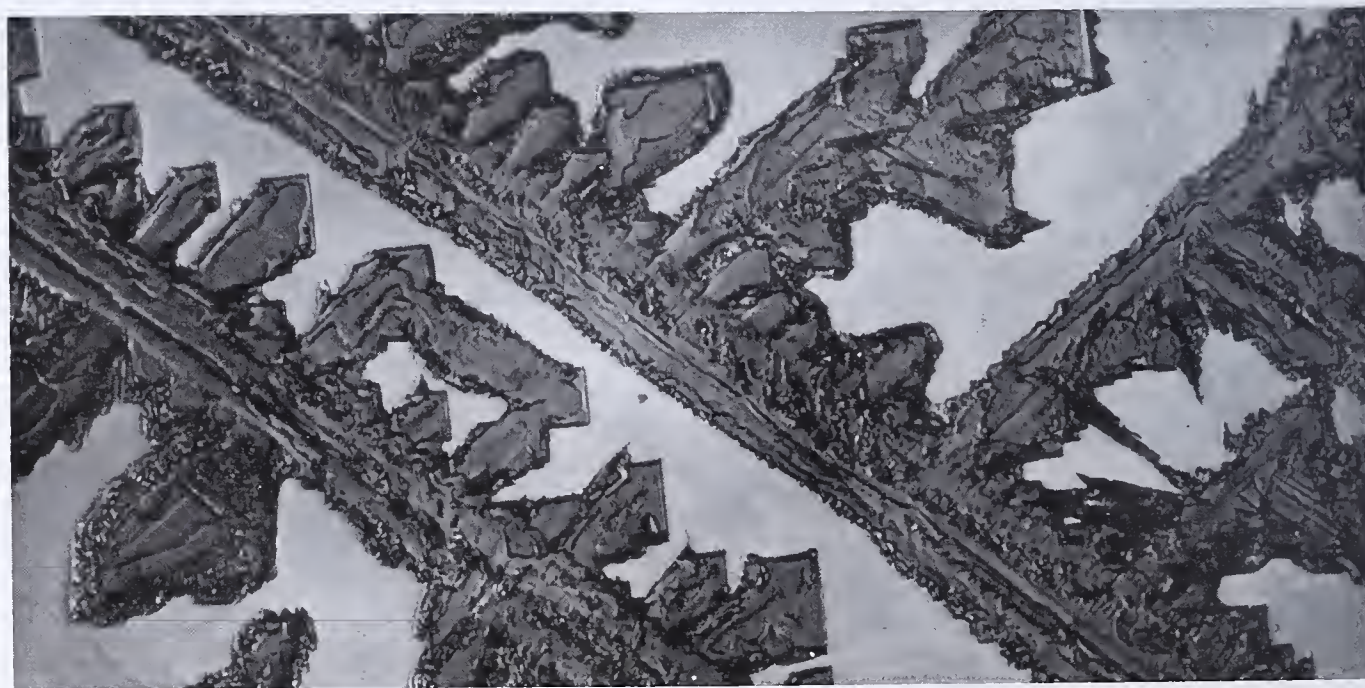
In Table II results obtained in analysis of soil extracts by these methods are given. These soil extracts were made with a molal solution of potassium chloride to which had been added enough acetic acid and ammonia to buffer it and make the pH 3.6 and the titratable acidity equal to 0.04 *N*. In these soil extracts other metals which may combine with dithizone, under the conditions described, were not present in appreciable amounts, except iron and manganese. Interference from those was prevented by addition of ammonium citrate.

Most quantities in Table II are averages of two or more separate determinations. There is some variation in the amount obtained from any soil by replicate extractions with potassium chloride solvent. Table II is included to illustrate applicability of the dithizone methods to examination of soil extracts, not to show what may be found in soils. It is planned to report upon soil zinc in another paper which will include much detail in respect to numerous soils.

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Courtesy J. T. Bryant and J. R. Rachele  
PHOTOMICROGRAPH OF QUINHYDRONE OF RESORCINOL AND BENZOQUINONE



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



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## Spectrographic Analysis of Biological Material

Lead, Tin, Aluminum, Copper, and Silver

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**T**ECHNICAL improvements developed during the past few years have greatly reduced the uncertainties attending quantitative spectrum analysis and have resulted in an increased application of emission spectrography to studies of trace metals in biological material (1-4, 6, 13, 14, 16, 19-21, 23, 26, 27, 29, 33, 34). The purpose of this paper is to present a method for the simultaneous determination of lead, tin, aluminum, copper, and silver in biological material and to call attention to certain improvements in procedure which have been introduced since the authors' earlier publications (2-4).

### Photometry

The earlier method of photometry (2, 3), which gave sufficiently accurate results (5) but was applicable only to relatively low concentrations of metals, has been replaced after a study of other techniques (10, 11, 13, 15, 28, 30) by the method of Preuss (25). This method, which employs the Hansen gage (17) to incorporate the blackening mark in the analytical spectrum, extends the analytical range, thereby reducing the dilutions otherwise required to handle relatively high con-

centrations of metals. However, a modification by means of which determinations of opacity could be substituted for determinations of density was found to be advantageous in the evaluation of very weak lines. This modification involves adherence to the authors' earlier method (2, 3) of dealing directly with faint lines instead of attempting to isolate and concentrate the test metal (2).

In applying the modification, the quantity of internal standard used must be such as to produce a standard line the density of which is below 0.30 (opacity of 2) in at least two steps of the spectrogram produced by means of the step sector. The measured opacities (galvanometer reading of emulsion/galvanometer reading of line) for the two weak steps of the standard line are plotted as a straight line against the relative exposures of the steps. The opacities for the test line are also plotted and the distance between the two lines at a base opacity (1.30) can then be correlated with the concentrations of the test metal (Figure 4). Figure 1 is a photograph of duplicate spectra with faint test lines and Figure 2 illustrates the method of obtaining the separations.

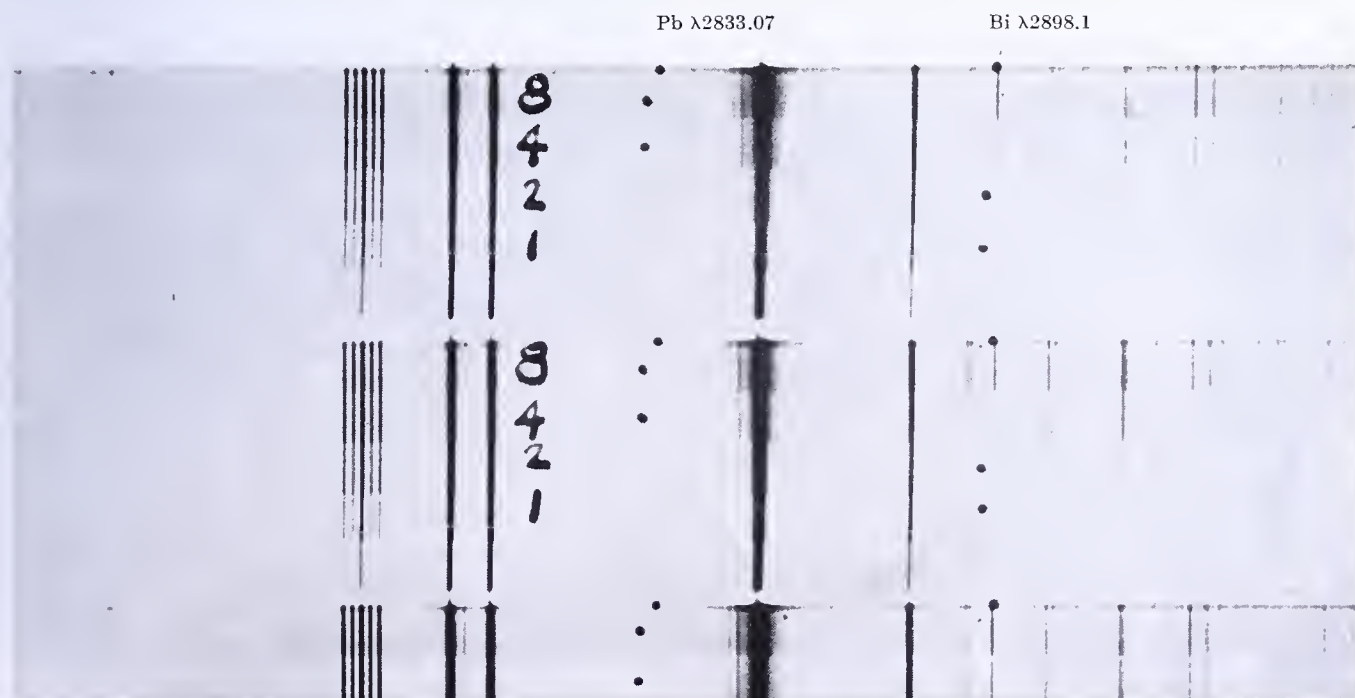


FIGURE 1



The foregoing procedure is employed in the case of spectrograms in which the test lines appear in not more than three exposure steps. When the line is present only in the maximum exposure step, the plot is made by assuming an opacity of 1.0 for the next lower step. When the test lines appear in three or more steps, the method is identical with that described by Strock (30) in which the intervals of separation

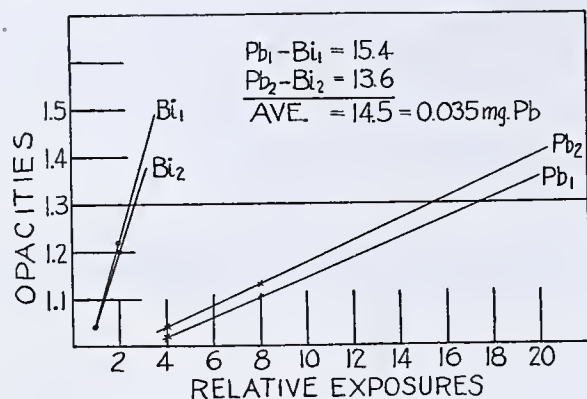


FIGURE 2

between the density curves for the test and standard lines at a base density of 0.30 are correlated with the logarithms of the concentrations (Figure 3). In borderline cases the choice of method depends upon whether or not the density curve for the test line can be accurately extrapolated to the base density of 0.30; when the density of the test line in the highest exposure step is less than 0.20, more accurate results can be obtained by resorting to the data on opacities.

### Apparatus

The spectral region employed (2600 Å. to 3500 Å.) is photographed with the large Bausch & Lomb quartz Littrow spectrograph, a spherical quartz lens being used between the slit and the light source. Persistent lines of magnesium, manganese, iron, nickel, chromium, and zinc which also occur in this region provide means for the inclusion of these metals within the scope of the method.

As in previous work (2-4) the source of excitation is a direct current arc between graphite electrodes. This source and its modification involving the cathode layer effect (22) are generally the most satisfactory means for volatilizing the minute quantities of metals usually encountered in biological material. Other sources, such as various sparking procedures (7, 8, 15, 16, 32), the alternating current arc (7, 9), the "Abreissbogen" (15), or the flame (21), result in a lowered sensitivity of detection which offsets the other advantages of their use.

The graphite electrodes (0.78 cm., 0.3 inch, in diameter) are prepared so that the positive rod, 40 mm. in length, contains a

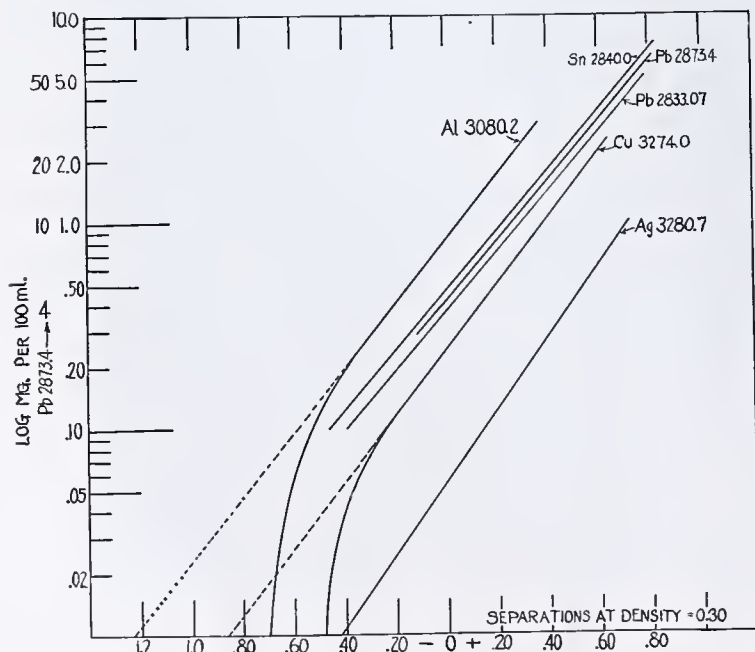


FIGURE 3

crater 3 mm. wide by 10 mm. deep into which the sample is introduced, while the negative, 70 mm. in length, is sharpened with a pencil sharpener to a fine point. This pointed electrode aids in centering and confining the arc, thereby reducing its tendency to wander.

Among other impurities, graphite electrodes, as purchased, contain aluminum and copper in such quantities as to necessitate their removal. Preliminary arcing for 1.5 minutes accomplishes this but also impairs the subsequent effectiveness of the electrodes because of increased arc wandering. A satisfactory method of purification consists in steeping the properly cut rods in a mixture of equal parts of distilled hydrochloric and nitric acids maintained at 70° C. over a period of 48 hours during which the bath is changed 4 or 5 times. This treatment is followed by a corresponding period of immersion in 4 or 5 changes of triple-distilled water also at 70° C., after which the electrodes are heated for 1 hour at from 900° to 1000° C. in an electric muffle furnace. Only boron, silicon, and traces of magnesium and vanadium then remain as impurities, and these may be reduced by other methods of purification (15, 18, 24, 35).

A sector for use in this work was designed with a relative exposure factor of 2 (log 0.30), in seven steps, each exposing a 2.5-mm. length of the slit of the spectrograph. The sector is provided with a slotted plate that can be adjusted to eliminate any number of steps. A five-step exposure was found to be the most practical and was used in this study. The sector exposes the slit over but one-third of its circumference. (Sectors with higher total exposures are useful in analyzing less persistent lines than those referred to herein. A suitable sector for such lines is one which is cut out on both sides so as to double the total exposure given the slit of the spectrograph.)

Density and opacity measurements were obtained with the Bausch & Lomb nonrecording densitometer. In order to measure 2.5-mm. sections of the spectrograms, it was necessary to increase the magnification by providing a longer arm for the projection mirror than that supplied with the instrument.

TABLE I. SPECTRAL LINES

Metal	$\lambda$ Line	Internal Standard	$\lambda$ Line
Lead	2833.07	Bismuth	2898.1
Lead	2873.4	Bismuth	2898.1
Tin	2840.0	Bismuth	2898.1
Aluminum	3082.16	Cobalt	3082.6
Copper	3273.96	Cobalt	3283.45
Silver	3280.67	Cobalt	3283.45

### Working Curves

The working curves may be obtained from solutions prepared by adding the test metals and the internal standards to a salt solution of such composition as to be readily adaptable to that of the materials handled, with respect to inorganic salts. The material chosen as the base was the synthetically prepared ash of normal urine as described elsewhere (2). A double internal standard, consisting of 5 mg. of bismuth and 100 mg. of cobalt per 100 ml. of solution, was employed. Table I lists the spectral lines of the metals and the corresponding lines of the internal standard, as used to derive the calibration curves.

Figures 3 and 4 illustrate the family of calibration curves used in this study. The extent of the analytical range for each line when used in either the density or opacity technique can be observed from the graphs.

### Preparation of Samples

The contaminations attending the chemical treatment of samples have been reduced to quantitative insignificance by employing purified acids and triple-distilled water (2) and by working in a laboratory equipped with a dust-removal system. Chemical treatments of the samples are preferred because they permit the use of solutions which in addition to guaranteeing the homogeneous nature of the samples greatly facilitates the introduction, into the craters of the electrodes, of the small amounts of material employed in the tests.

Urine samples are prepared for analysis by the method described previously (4), except that the mixed internal standard (1 ml. = 0.5 mg. of bismuth and 10.0 mg. of cobalt) is added.



TABLE II. CONCENTRATIONS OF METALS IN HUMAN TISSUES  
(Case A. P. 1937. Age 75 years)

Tissue	Sample <i>Grams</i>	Metal Found				
		Pb	Sn	Al	Cu	Ag
		<i>Mg. per 100 grams fresh tissue</i>				
Kidney	50.0	0.02	0.015	0.02	0.20	0.00
Heart	50.0	0.015	0.015	0.06	0.18	0.00
Brain	51.8	0.015	0.00	0.002	0.45	0.005
Stomach	50.0	0.03	0.02	0.14	0.09	0.00
Liver	50.0	0.14	0.03	0.02	0.55	0.00
Spleen	50.0	0.035	0.02	0.12	0.09	0.00
Small intestine	32.0	0.025	0.025	0.10	0.09	0.00
Skin	13.0	0.025	0.015	0.075	0.04	0.00
Lung	50.0	0.03	0.055	6.60	0.07	0.015
Colon	25.0	0.025	0.025	0.12	0.05	0.01
Blood	13.0	0.025	0.00	0.45	0.11	0.00
Urinary bladder	24.0	0.01	0.01	0.065	0.06	0.005
Gall bladder	5.4	0.015	0.00	0.02	0.17	0.005
Muscle	10.0	0.005	0.00	0.04	0.10	0.00
Rib	5.2	0.39	0.00	0.01	0.21	0.00
Femur	9.2	3.59	0.00	1.09	2.50	0.00

Other biological materials, excepting spinal fluid, are prepared for analysis by ashing in silica dishes at a temperature not exceeding 500° C. The dried material is ashed directly or after digestion with distilled nitric acid. The latter procedure reduces the time required for ashing and was employed for all materials excepting feces, which are ashed after drying to constant weight (2). Complete destruction of organic matter may be hastened further by treating the grayish ash with a little distilled nitric acid (1 to 1), evaporating to dryness, and replacing in the muffle furnace for a few minutes. The ash is dissolved in distilled nitric acid and triple-distilled water. In the case of feces and food samples sufficient distilled hydrochloric acid is added to prevent the formation of meta-stannic acid. From this point the procedure is the same as previously described, the method of "excess" being employed to alter the solutions so that they conform (within certain limits) to the inorganic salt composition of the salt base adopted for deriving the calibration curves (2). [The diluent used for this purpose consists of 50 ml. of the salt stock (2), 5 mg. of bismuth, 100 mg. of cobalt, and sufficient triple-distilled water to make the volume 100 ml.] Two-tenth milliliter portions removed with a capillary pipet are placed in the craters

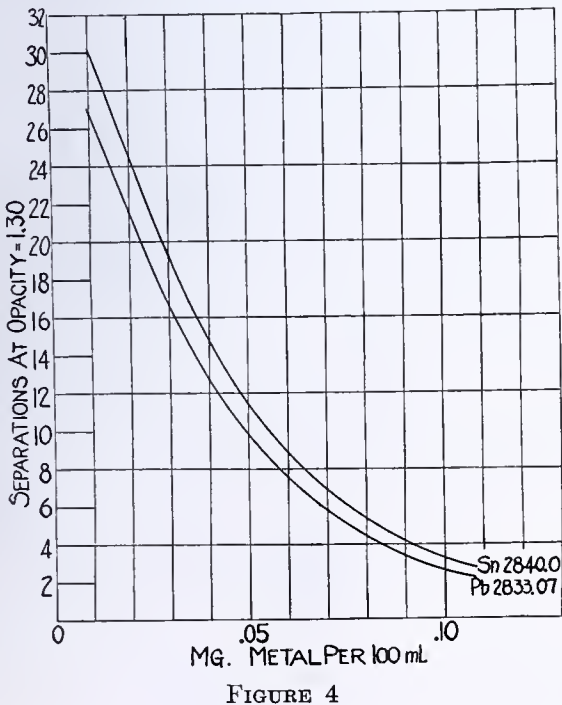


FIGURE 4

of each of two purified electrodes and arced for 2 minutes, the data for the two spectrograms being averaged to determine the quantities of the metals present. In order to avoid contaminations or losses in handling small samples of spinal fluid, the manipulations are kept at a minimum. The procedure is to collect or place the sample in a graduated 15-ml. quartz centrifuge tube, note the volume, add 0.1 ml. of distilled nitric acid for each 1 ml. of spinal fluid, and concentrate in a water bath to one-tenth of the original volume. Following the addition of an equal volume of the salt diluent, 0.4-ml. portions are placed in the electrodes and their arc spectra are photographed. Such a procedure permits duplicate analyses of samples as small as 5 ml. in which as little as 0.05 gamma of each metal can be determined quantitatively.

Results

In Tables II and III are recorded the findings for a complete series of necropsy specimens and for a number of other materials handled in the laboratory. The accuracy of the technique can be observed from the results listed in Table IV, in which are given the recoveries on duplicate samples prepared by adding known amounts of the metals to the base salt stock.

TABLE III. CONCENTRATIONS OF METALS IN BIOLOGICAL MATERIAL

Material	Metal Found				
	Pb Mg.	Sn Mg.	Al Mg.	Cu Mg.	Ag Mg.
Spinal fluid	<0.001/100 ml.	0.000/100 ml.	<0.00/100 ml.	0.001/100 ml.	0.000/100 ml.
Feces					
R. (24 hr.)	1.12	3.00	5.20	0.94	0.04
R. (24 hr.)	2.00	12.40	8.00	2.00	0.02
G. (24 hr.)	0.56	3.00	7.00	1.04	0.03
Food (composite) <sup>a</sup>	0.15	3.75	1.55	1.59	0.02
	0.27	1.12	3.10	1.85	0.02
	0.35	7.80	12.00	2.34	0.07
Mg. per liter					
Urine					
R.	0.04	0.015	0.03	0.06	0.00
D.	0.015	0.00	0.09	0.06	0.00
G.	0.06	0.00	0.05	0.06	0.00
Mg. per 100 grams					
Blood					
R.	0.055	0.00	0.10	0.17	0.00
D.	0.025	0.00	0.005	0.13	0.00
G.	0.04	0.00	0.02	0.13	0.00
Liver J. M.	0.12	0.10	0.12	0.50	0.01

<sup>a</sup> This represents an exact duplicate of subject's food intake over 24-hour period.

In order to reduce the effects of mutual contaminations in the individual standard metal solutions, the lowest concentration of each metal was made somewhat higher than that encountered in practice. Results which are reported as 0.00 in Tables II and III do not signify that these metals were absent but only that the quantities present were less than 0.005 mg. per 100 grams of tissue; in the case of silver very faint lines could be seen, but occasionally the presence of the tin line was doubtful.

TABLE IV. RECOVERIES OF KNOWN AMOUNTS OF METAL ADDED TO BASE SALT SOLUTIONS

Lead		Tin		Aluminum		Copper		Silver	
Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
0.05	0.04	3.00	2.90	1.00	1.20	0.30	0.27	0.02	0.03
	0.05		3.30		1.00		0.28		0.025
0.30	0.32	0.03	0.03	0.30	0.26	1.50	1.33	0.20	0.18
	0.31		0.03		0.27		1.40		0.22
2.00	1.85	0.40	0.36	0.03	0.02	0.10	0.085	0.60	0.66
	1.95		0.38		0.02		0.085		0.70
5.00	4.70	5.00	5.20	8.00	8.75	0.03	0.03	0.10	0.085
	4.90		4.70		8.75		0.03		0.10

Discussion

Figures 3 and 4 show that, of the metals studied, lead and tin must be determined with reference to the opacities of the spectral lines when present in quantities below 0.10 mg. per



100 ml. of solution. The test lines of aluminum, copper, and silver are so persistent that their densities can be used over their entire analytical ranges. In the case of copper and aluminum very small quantities present as impurities in either the internal standards or the base salt stock markedly influence the respective curves in the lower analytical ranges. This effect decreases as the concentration of the test metal increases and, moreover, it can be determined and compensated for by extrapolating the straight portions of the curves, as shown by the dotted lines in Figure 3.

The base salt stock and the cobalt internal standard stock used in these observations provided contaminations to the extent of 6% of copper and 12% of aluminum per 100 ml. of solution. Treatment of the salt stock with hydrogen sulfide (2) removes all but minute quantities of copper, which may be further reduced by treatment with sodium diethyldithiocarbamate (31). The chief source of contamination with copper, however, was the cobalt internal standard (Mallinckrodt's analytical reagent cobalt chloride) purification of which by sodium diethyldithiocarbamate or by a dithizone treatment (12) did not prove successful. By means of the former reagent, cobalt is precipitated and extracted with the copper, in the ether (or chloroform) layer, while in the case of the latter reagent the large excess of cobalt over copper prevents the extraction of the copper. The chief source of contamination with aluminum is the salt stock. Thus far, suitable methods for the elimination of this factor have not been found. It is obvious, therefore, that in the case of aluminum it is necessary to determine the magnitude of the contamination due to the salts each time the stock salt solution is renewed from new lots of salt. Since excess salts are not added to urine samples, quantities of aluminum below 0.20 mg. per 100 ml. of solution can be determined by applying the extrapolated line.

It is possible to extend the analytical range for certain of the metals by employing suitable less persistent lines, as in the case of lead, for which the line at  $\lambda 2873.4$  is employed at concentrations above 4.0 mg. per 100 ml. of solution (Figure 3). Tin, when present in amounts less than 10 mg. per 100 ml. of solution, also gives a number of lines in the spectral region studied, but their persistencies are so little less than that of the  $\lambda 2840$  line as to give little benefit from their use. Only a few lines of aluminum and copper are visible, the aluminum line at  $\lambda 3092.8$  being useless because of the presence of a magnesium line at  $\lambda 3093.05$ . The copper line at  $\lambda 3247.55$  is probably more persistent than the line at  $\lambda 3274$  but, since the former falls in a region in which a number of narrow bands occur, the latter line is measured with greater ease when minute amounts of copper are present. The only silver line produced by concentrations within the range likely to be encountered was that at  $\lambda 3280.67$ .

High concentrations of aluminum provided the only serious difficulties in the analyses. Such samples required further dilution and repeated spectrograms. After some experience with the materials to be handled, it was found that fecal and food samples which usually contained the largest quantities of aluminum, as well as relatively larger amounts of the other metals, could be so adjusted in the final volumes as to permit the complete analysis from a single spectrogram. Only in the case of lung samples which usually contained traces of lead, tin, copper, and silver and appreciable quantities of aluminum was it necessary to make separate analyses for aluminum.

In preparing the samples of known metallic content shown in Table IV, it was found that silver chloride was precipitated when silver in excess of 0.10 mg. per 100 ml. was present. So long as the precipitate was finely dispersed, no difficulty was encountered in making the analyses if the portion to be mixed with the diluent was removed immediately after vigorous

shaking of the solution. When heavy precipitates were present they could be dissolved by the addition of 1 to 2 ml. of 5 per cent sodium thiosulfate solution. Thus far such amounts of silver have not been encountered in biological material.

With the calibration curves starting at 0.01 mg. per 100 ml. of solution, and by adjusting the final volumes of the dissolved ashed material to one-half or even one-fourth of that previously recommended (2), it is frequently possible to determine amounts of metal as low as 0.0025 to 0.005 mg. per 100 grams of fresh material.

## Summary

A spectrographic method is described for the simultaneous determination of lead, tin, aluminum, copper, and silver in biological material. Important improvements in the method include the use of graphite electrodes which are purified by means of a chemical treatment; the use of a step sector which when employed to incorporate the blackening mark in the analytical spectrum also enables a considerable extension of the analytical range; and the use of opacities in place of densities, which improves the accuracy of evaluating faint spectral lines.

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# The Determination of Rhenium

## Estimation in Pyrolusite

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An analytical method for the determination of rhenium in the presence of large amounts of manganese dioxide has been developed and demonstrated on synthetic mixtures. Analysis of a representative group of pyrolusite samples from many parts of the world indicated that the naturally occurring mineral contains inappreciable amounts of rhenium. The highest concentration observed was 0.2 part per million parts of mineral.

THE presence or absence of rhenium in manganese minerals in general and pyrolusite in particular has been a controversial question since the time of the discovery of the element. Although it has been shown (4) that some early methods used for isolating rhenium from manganese concentrates were unreliable and that manganese compounds in general ordinarily contain inappreciable amounts of the element, evidence indicated that pyrolusite from selected sources contained small but definite amounts of rhenium.

During an earlier spectrographic examination (7) of the acid-insoluble sulfide concentrates obtained from a few samples of western American pyrolusite, evidence was obtained which indicated the presence of rhenium. Routine examination of about fifty random samples of widespread geographic origin revealed its presence in twenty-two specimens. Identification was in most cases based upon one or two lines and it was known that concentrations were on the border line of the sensitivity of the method. It was not fully realized at that time that any method involving identification based upon the appearance of one line of the 3460 Å. triplet or the 4880 Å. line was hazardous because of the virtual coincidence of iron, manganese, and molybdenum lines, some of which were not recorded in the conventional atlases.

All the samples available for the study had been previously analyzed for elements known to be detrimental in dry cells of the Leclanché type and with one or two exceptions were found to have normal compositions. Because it is axiomatic in the dry-cell industry that a chemical analysis of a given pyrolusite does not necessarily prognose its behavior in a cell, all samples had been tested as dry-cell depolarizers. About half of the samples were of such a nature that the cells in which they were incorporated had subnormal shelf lives and were deficient on drain tests. When the results of the spectrographic examination were compared to the electrical data, with but three exceptions the samples thought to contain rhenium were unsatisfactory as dry-cell constituents.

Because of this striking correlation, samples of high-grade Montana pyrolusite were compounded with rhenium dioxide to yield products containing 0.075, 0.0075, and 0.00075 per cent of rhenium. The materials along with uncontaminated ore were incorporated in dry cells which were subjected to intermittent and continuous drain tests. It was found that the cells containing rhenium were inferior to the controls in

every respect and that the deficiencies were in proportion to the rhenium concentrations. Figure 1 illustrates the condition of the inner surfaces of the zinc cans at the end of 72 hours of intermittent drain through 80 ohms. It was evident that the presence of rhenium in pyrolusite was objectionable if the mineral was to be used in the construction of Leclanché cells. The need for an adequate method of quantitative analysis was likewise apparent.

An added stimulus to the development of a method for the analysis of rhenium in the presence of large amounts of manganese lies in the possibility that, if a naturally occurring manganese ore containing rhenium, element 75, can be found, element 43 will likewise be present. The repeated failure of investigators to confirm the isolation and identification (11) of the middle homolog of the manganese-rhenium series lends support to the view that its properties are as yet unknown.

### Historical

Two general methods have been proposed for the isolation of rhenium from manganese concentrates. Those procedures involving manipulations based upon an assumed similarity

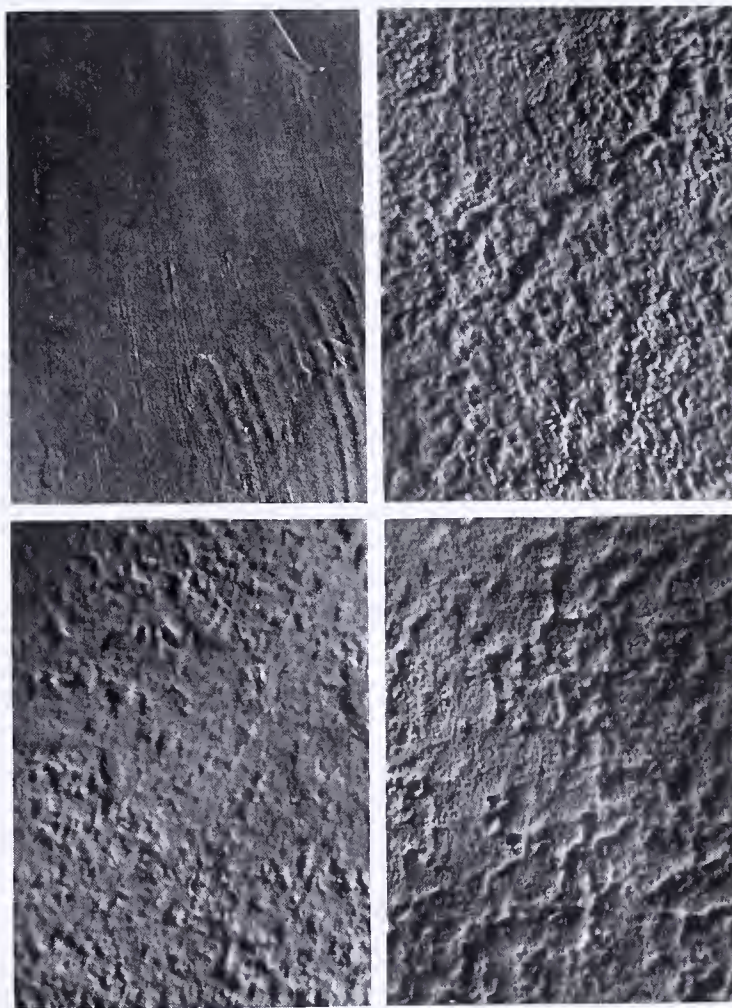


FIGURE 1. RHENIUM IN PYROLUSITE

Upper left. Blank  
Upper right. 0.00075 per cent rhenium  
Lower left. 0.0075 per cent rhenium  
Lower right. 0.075 per cent rhenium

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of rhenium to manganese have been previously discussed (4). The results reported by the discoverers of the element (10) indicate that manganese minerals contain no rhenium. Unfortunately the analytical procedure followed in the examination of the eighteen hundred odd miscellaneous minerals reported was not clearly disclosed. Whether or not the manganese-containing samples were analyzed by alternate oxidation and reduction of the sample, followed by x-ray examination of the sublimes, is not definitely known. Since this procedure was followed in the majority of the cases, it is probable that the same technique was applied to the hausmannite, rhodonite, psilomelane, and hauerite specimens. If so, the values reported are without significance. In the presence of a large excess of basic material only a fraction of the rhenium present in a sample may be removed by this treatment. When the sample is reduced in a hydrogen atmosphere, metallic rhenium is formed. This is nonvolatile under ordinary conditions. Upon introducing oxygen into the system, the rhenium is oxidized to rhenium heptoxide, which in the absence of bases is volatile. In the presence of the hundred thousand fold excess of basic oxide encountered in actual samples, the heptoxide reacts to form essentially nonvolatile perrhenates. It is not to be expected that substantial percentages of the rhenium present will escape during the alternate reduction and oxidation and the prediction may be readily substantiated by experiment.

In one series of experiments conducted by the senior author, manganese dioxide was moistened with sufficient potassium perrhenate solution to yield samples which when dry contained 0.1, 0.01, and 0.001 per cent of rhenium. Fifty-gram samples of the mixtures were heated alternately in oxygen and hydrogen at 600° C. The sublimes and condensates were collected in a trap cooled with acetone and carbon dioxide snow. Between oxidation and reduction the system was swept out with nitrogen. Each cycle required 2 hours and three complete cycles extending over 6-hour periods were carried out in duplicate on each sample. Condensates in the tube and trap were washed out with 5 per cent sodium hydroxide to which hydrogen peroxide was added. Analysis of the extracts indicated the presence of between 70 and 10 micrograms of rhenium in the two richest samples and none in the most dilute sample. Similar analysis of a series of pyrolusite, columbite, wulfenite, rhodochrosite, hausmannite, and keilhauite specimens by Noelck (12) had previously failed to reveal the presence of rhenium. It was evident that but a minute fraction of the rhenium present was recovered by the treatment and that the possibility existed that manganese minerals might contain rhenium which would not be detected when the minerals were analyzed according to the Noddack method.

The most sensitive method yet developed for the estimation of rhenium is that of Geilmann (2). Inasmuch as the variables of this method had been established over the ranges encountered in ordinary analytical work (6), it was used as a basis for the present procedure. In addition to molybdenum, the interference of which was to be expected when dealing with pyrolusite samples, chloroplatinic acid responds to the stannous chloride-thiocyanate treatment to yield an ether

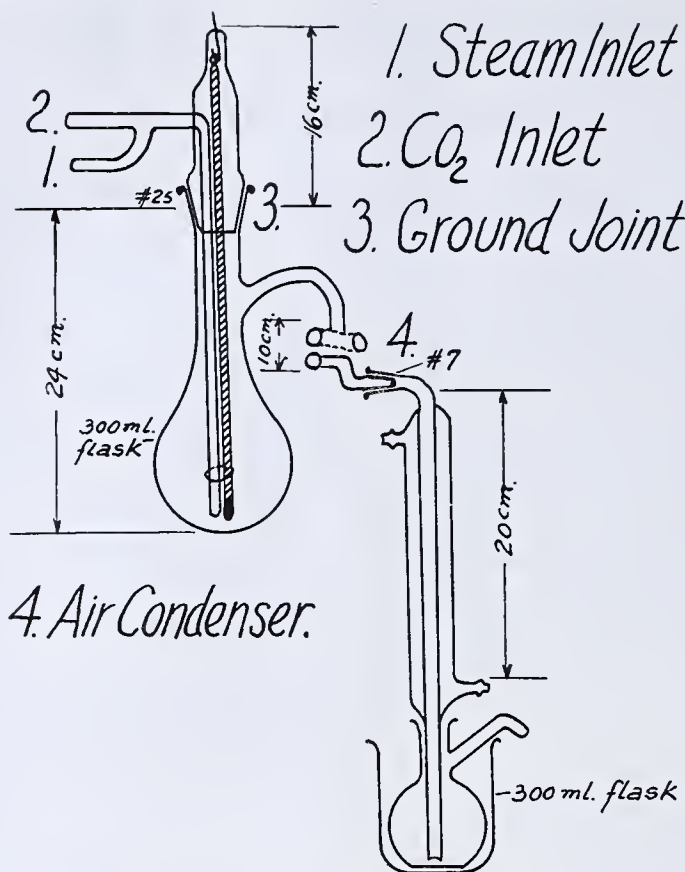


FIGURE 2. DISTILLATION SETUP

extract having a color somewhat similar to that of rhenium. Any procedure involving final estimation of the rhenium by the standard colorimetric method must make adequate provision for the separation of the two interfering elements. Separation of rhenium from large amounts of molybdenum may be accomplished by a steam distillation from a sulfuric acid solution. The original method of Geilmann (1) involving distillation in a stream of moist hydrogen chloride has been modified by Kronmann (8) and Noddack (9). Direct distillation of small amounts of rhenium from concentrated acid solutions of manganous sulfate is not practical because of the mechanical difficulties encountered when large amounts of anhydrous manganous sulfate separate out during the distillation.

The determination as finally developed consisted of a combination of the colorimetric and distillation methods. Because the various steps leading up to the final estimation have never been investigated under the conditions peculiar to the type of sample under consideration, it was necessary to check each step individually. The principal operations involved are solution of the pyrolusite, extraction of rhenium and molybdenum, solution of the extract, separation of the rhenium from the bulk of the molybdenum by distillation, and colorimetric estimation of the rhenium in the distillate.

## Experimental

**SOLUTION OF SAMPLE.** When manganese dioxide or potassium permanganate is digested with hydrochloric acid in the presence of potassium perrhenate there is no appreciable loss of rhenium (3). Although the results reported were on samples of such size that the gravimetric sulfide-nitron method could be used, a similar set of data indicated that when smaller amounts were dissolved under similar conditions the variations in apparent recoveries were of the same order as the precision of the colorimetric method of analysis. The presence of a ten thousand fold excess of manganese did not interfere with the extraction. As a matter of precaution, all samples of pyrolusite involved in the preliminary experiments and in later analyses were dissolved and digested at temperatures below 80° C. in large Erlenmeyer flasks.

**EXTRACTION.** Rhenium and molybdenum were extracted by adding stannous chloride to the hydrochloric acid solutions of manganese chlorides in amounts sufficient to reduce all ferric and manganic salts present. Stannic chloride has been shown to be without significant influence upon the intensity of the color produced (6). When reduction of the salts to the divalent state was evidenced by the change from a yellow-orange to the clear pink of manganous chloride, enough 20 per cent potassium thiocyanate solution was added to give a concentration of 0.5 gram per 100 ml. of solution. This was followed by 20 per cent stannous chloride sufficient to provide 0.6 gram per 100 ml. The solution was shaken in a separatory funnel and after 7 minutes was extracted with successive portions of ether until a practically colorless ether layer was obtained. Four 60-ml. portions were generally sufficient.



Oxidation of the rhenium oxythiocyanate extract was one of the most critical steps in the procedure. If the combined extracts were evaporated to dryness, decomposition of the complex compound usually followed and an objectionable residue remained. The best results were obtained if the bulk of the ether was removed by evaporation over a water bath. When but 5 to 10 ml. remained, 15 ml. of hydrochloric acid (1 to 1) were added and the remainder of the ether was removed by blowing a jet of air across the surface of the liquor. Hydrogen peroxide (30 per cent) was then added to oxidize the rhenium to perrhenic acid. Although alkaline hydrogen peroxide yielded a colorless solution, its use was objectionable because of the tendency of such solutions to precipitate sulfur when acidified for distillation. Potassium chlorate in acid solution and hydrogen peroxide in neutral solution were not as satisfactory. Unless the oxidation was carried out in such a manner as to yield a colorless solution free from sulfur, low results were obtained.

**DISTILLATION.** The distillation of rhenium from sulfuric acid solutions of the oxidized extract was studied in the presence and absence of hydrogen chloride. It was observed that quantitative recoveries of 200-microgram amounts of perrhenic acid could not be made using the conventional distillation method. Accordingly, a large number of determinations were made in which the rate of distillation, the volume of hydrochloric acid, the volume of water, and the temperature of distillation were varied. Finally carbon dioxide was substituted for the hydrogen chloride and the method modified in the following manner:

The rhenium as perrhenate was placed in the distilling flask along with 150 to 250 ml. of 98 per cent sulfuric acid. The contents of the flask were heated to between 270° and 290° C. and maintained at this temperature while steam and carbon dioxide were passed through at such a rate as to ensure the distillation of about 250 ml. in 2 hours. The carbon dioxide flow was regulated so that the volume was from one-third to one-half that of the steam. In Table I is to be found a summary of the results obtained on the analysis of fifty-one consecutive samples.

TABLE I. DISTILLATION OF RHENIUM				
No. of Samples	Rhenium Taken	Rhenium Found (Av.)	Maximum Deviation	Average Deviation
	γ	γ	γ	γ
10	25.0	25.2	5.2	1.8
9	50.0	50.9	4.1	2.5
11	100	102	12	4
15	200	201	9	3
6	500	491	29	14

Determinations carried out on pure molybdic oxide under the same conditions indicated that when as much as 10 grams was added to the distilling flask the distillate never contained over 0.5 mg. of molybdenum. Inasmuch as the preliminary extraction of digested pyrolusite samples had at no time indicated the presence of such large quantities of molybdenum, it was assumed that the possibilities of interference were slight.

**ESTIMATION.** Because the previous investigations on the effect of sulfuric and hydrochloric acids upon the development of the rhenium (6) and molybdenum (5) colors were not extended into the high concentration ranges encountered in distillates of the Geilmann-Weibke type, it was necessary to determine the effect of these variables before attempting to evaluate the efficiencies of various modifications of the conventional distillation.

A study of the effect of hydrochloric acid upon the intensity and stability of the colors produced by optimum amounts of stannous chloride and potassium thiocyanate in acid concentrations between 0.2 *N* and 9.15 *N* indicated that whereas the rhenium complex was remarkably stable in 4 *N* hydrochloric acid, the molybdenum color was almost completely bleached in 12 minutes. In 4.5 *N* hydrochloric acid the color produced by molybdenum was negligible at the end of 6 minutes, whereas the rhenium color was unaffected. Sulfuric acid in concentrations between 1 *N* and 12 *N* was

found to have much less effect upon the intensity of color produced with 400 micrograms of rhenium and 400 micrograms of molybdenum than corresponding concentrations of hydrochloric acid. The rhenium-containing solutions reached their maximum intensity in 10 *N* sulfuric acid. It therefore seemed possible that in mixed hydrochloric-sulfuric acid solutions of proper concentration the development of color due to the molybdenum thiocyanate complex could be inhibited without greatly altering the extent of the rhenium reaction. Optimum concentrations appeared to be 9.3 *N* sulfuric acid and 4.9 *N* hydrochloric acid. Accordingly, colorimetric comparisons were made to ascertain whether or not rhenium could be determined in the presence of molybdenum and if so what the approximate concentration limit of molybdenum was. Two hundred micrograms of rhenium as perrhenate and varying amounts of molybdenum as molybdate were added to 75 ml. of mixed acid of the above concentrations. Stannous chloride and potassium thiocyanate were added in the proper amounts, and at the end of 6 minutes comparison was made with similar solutions containing no molybdenum. In Table II are to be found the results obtained.

TABLE II. EFFECT OF MOLYBDENUM				
Molybdenum Added	Rhenium Added	Estimated	Molybdenum Added	Rhenium Estimated
γ	γ	γ	γ	γ
200	200	198	1000	200
200	200	196	1000	207
200	200	202	1000	204
400	200	201	2000	225
400	200	201	2000	232
400	200	200	2000	240

In acid concentrations as high as those used, the various organic solvents such as ether, butyl acetate, or cyclohexanol which are ordinarily employed as extractors in the determinations cannot be used. Not only is their solubility greatly increased by the presence of so much acid, but when extraction is made the molybdenum reaction is reversed. Colorless solutions containing molybdenum but no rhenium will upon extraction yield colored nonaqueous solutions, the concentration of which varies directly with the number of extractions.

It was concluded that, since the amount of molybdenum distilling over with the rhenium did not exceed 2 mg., a direct colorimetric estimation could be made, provided the acidities were properly adjusted.

Procedure

The composite procedure as finally developed was as follows:

One hundred grams of finely pulverized pyrolusite were placed in a 1-liter Erlenmeyer flask and moistened with 50 ml. of water and 200 ml. of hydrochloric acid (sp. gr. 1.2) were added as rapidly as the frothing and the energetic reaction would permit. After the initial reaction had subsided, the flask was placed on a hot plate and warmed to 60° to 80° C. Solution required 8 or more hours and it was usually necessary to make small additions of acid from time to time. When the reaction was complete, the silica and insoluble matter settled out as a light yellow sand and the solution was free from suspended matter. After cooling, the sample was diluted to about 300 ml. and filtered on a Büchner funnel. The precipitate and the filter paper were returned to the flask and 10 to 15 ml. of water were added, followed by 25 ml. of hydrochloric acid (sp. gr. 1.2). The liquid was heated to boiling and filtered. The two filtrates were united and placed in a separatory funnel.

A 20 per cent stannous chloride solution was then added in small portions until all ferric and manganic compounds were reduced to the divalent state. To the resulting clear pink solution 20 per cent potassium thiocyanate was added in amounts to yield a solution containing 0.6 gram per 100 ml. This was followed by reducing agent in sufficient quantity to yield a solution containing 0.5 gram of stannous chloride per 100 ml. After 7 minutes, during which time the funnel was shaken several times, 60 ml.



TABLE III. DETERMINATION OF RHENIUM

No.	Rhenium Added P. p. m.	Rhenium Found P. p. m.	Error P. p. m.
1	0.2	0.3	0.1
2	1.1	1.0	0.1
3	0.0	0.0	0.0
4	0.8	0.7	0.1
5	1.4	1.7	0.3
6	0.3	0.3	0.0
7	0.2	0.3	0.1
8	1.8	1.7	0.1
9	0.0	0.0	0.0
10	2.1	2.2	0.1
11	0.3	0.3	0.0
12	0.0 (100 Mo)	0.0	0.0
13	2.0	1.4	0.6
14	1.7	1.3	0.4
15	0.6	0.6	0.0
16	0.0 (100 Mo)	0.0	0.0
17	1.4	1.0	0.4
18	0.9	0.6	0.3
19	1.9	1.5	0.4
20	0.4	0.4	0.0

of ethyl ether were added and the combined rhenium and molybdenum oxythiocyanates were extracted. Four successive 60-ml. portions of ether were generally required to remove the colored complexes completely.

The combined extracts were transferred to a distilling flask which was immersed in a water bath maintained at 70° C. and all except 5 to 10 ml. of the solution were removed by distillation. To the concentrated extract 15 ml. of hydrochloric acid (sp. gr. 1.1) were added and the remaining ether was removed with a gentle current of air impinged on the surface of the residue. Hydrogen peroxide (30 per cent) was then added drop by drop until all brown, red, or orange color disappeared. It was then allowed to stand for 10 to 15 minutes, hydrogen peroxide being occasionally added to prevent the return of any tinge of color. The solution was then diluted to 200 ml. with sulfuric acid (sp. gr. 1.8) and transferred to a distilling flask of the type illustrated in Figure 2. The temperature of the flask was raised to 270° to 290° C. and steam and carbon dioxide were passed through the solution over a period of 2 hours until 250 ml. of distillate were condensed in an ice-cooled receiver. The specific gravity of the distillate was in the neighborhood of 1.15.

Usually the distillates had a faint odor of sulfur dioxide. If the odor was pronounced and accompanied by the deposition of sulfur, improper oxidation of the extract was indicated and low results were obtained. In order to destroy the sulfur dioxide, bromine vapor was then bubbled through the distillate until it acquired a faint yellow color. The specific gravity of the acid solution was determined and a series of standards containing 50, 100, and 200 micrograms of rhenium (as potassium perrhenate) in 250 ml. of dilute sulfuric acid of the same density as the distillate was prepared. To each of the standards and the sample 100 ml. of hydrochloric acid (sp. gr. 1.2) were added. After cooling, 10 ml. of 20 per cent potassium thiocyanate and 15 ml. of 20 per cent stannous chloride were added to each solution. After thorough mixing aliquots were taken and the colors compared in 100-ml. Nessler tubes. From the volume of a given standard required to match an aliquot of the sample, the amount of rhenium in the original pyrolusite could be estimated.

Figure 3 shows a bank of stills used in the routine analysis of ores and concentrates.

Table III presents the results obtained by one of the authors (C. H.) on a set of samples prepared by adding known amounts of rhenium to 100-gram samples of rhenium-free western pyrolusite. The concentrations were unknown to the operator.

It was fully realized that the per cent error involved in some of the determinations was exceedingly high. However, in the light of the many involved operations, the large sample required, and the small amount of rhenium present, the deviations are understandable.

### Analysis of Samples

A total of 80 samples of pyrolusite from Arkansas (13), Alabama (4), Arizona (2), California (1), Colorado (6), Idaho (4), Virginia (5), Montana (15), North Dakota (1), Tennessee (1), Wyoming (1), Africa (4), Brazil (4), Bulgaria

(1), Dominican Republic (1), Egypt (2), Mexico (5), Nova Scotia (1), Russia (4), Siam (1), and four of unknown origin was analyzed in duplicate according to the method described above. In the majority of the samples no rhenium was found. Three samples of low-grade Montana ore contained 0.1 p. p. m. and one was found to contain 0.2 p. p. m. Four of the five Mexican samples contained 0.1 p. p. m.



FIGURE 3. BANK OF STILLS USED IN ROUTINE DETERMINATION OF RHENIUM

It is to be concluded that within the limits of the method pyrolusite ordinarily contains no rhenium. Whether or not the amounts found in a few of the specimens analyzed were large enough to be of significance in the industrial applications of the ore can be established only by further investigations.

### Acknowledgment

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# Measurement of Refractive Indices of Resins and Plastics

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IN A PAPER on the measurement of refractive indices of resins, Bradley (1) mentioned the Abbe refractometer as being "sometimes desirable." A later writer (3), while calling for a simple method of making these measurements, dismissed this instrument with the sentence, "The Abbe type of refractometer is not suitable, because most resins melt between 70° and 200°."

In this note, based on experience with a standard Bausch & Lomb instrument, the Abbe refractometer is shown to be in fact suitable for measuring refractive indices of a variety of resins and similar transparent plastic materials that fall in its range, including those that soften only above 70° C.

The total reflection method requires that the specimen have one smooth flat surface. It will only rarely be necessary to cut and polish this surface; generally it will be simpler to form the surface because the materials in question are organic glasses that are plastic by nature. For example, the material may be dissolved in a volatile solvent and the solution allowed to dry on a flat surface, or it may be melted and cooled on a flat surface; an oxidizing oil may be allowed to dry, or a heat-convertible resin may be baked on a flat surface, etc. The flat surface is sometimes the Abbe prism itself, but this is often inconvenient; for the material may dry or cure slowly, which would tie up the instrument, the softening point or baking temperature may be high, which would put too great a strain on the expensive prism, or the material may tend to chip the prism. In such cases it is plainly preferable to form the material on a flat surface other than the Abbe prism, and one with which greater liberties may be taken.

A smooth film may be cast from solution onto any flat surface, and after drying may be measured film side down on the Abbe without removing from the support. In this way, for example, the cleared gelatin layer of a photographic plate may be measured.

It is not necessary, however, to go to the trouble of forming a smooth film. If the material is formed on a piece of glass of higher refractive index than the material, and having plane parallel faces, the free side of the flat may be placed in contact with the Abbe prism using a suitable liquid and the reading made in the usual manner. Microscope slide glass is satisfactory for the few resins, such as vinyl acetate, of refractive index less than that of the crown glass of which the slides are made ( $n = 1.51$  to  $1.52$ ). Most resins, however, have a higher refractive index than crown glass; for these it is necessary to obtain flint glass flats. A rectangular form about  $2.5 \times 1.25 \times 0.075$  cm. thick ( $1 \times 0.5 \times 0.030$  inch) is satisfactory, and if the refractive index is about 1.63 it will take care of the majority of natural and artificial resins and plastics; to dispose of the whole range of the Abbe, the flats should, of course, have the same refractive index as the prism.

Any specimen prior to measurement is best examined in a polariscope to determine whether it is isotropic or birefringent, and in the latter event to find the character of the birefringence with a suitable compensator plate.

To increase the accuracy of the measurement of a material not formed on the Abbe prism but left on a separate support, two readings should be made; the second is made after rotating the specimen in the plane of its flat surface through 180° from the first position. This is easy if the support is rectangular in outline.

The light path in the Abbe may follow one of three courses: The light may be admitted through the front opening of the refracting prism (reflection position); through the back or accessory prism (transmission position); or through the edge of the specimen itself. The second position is commonly used for liquids, the third for solid specimens of appreciable thickness; both give a stronger contrast at the critical edge than the first position. The following discussion is confined to the first or reflection position, because it is more convenient and more generally applicable to the materials under consideration, especially when the specimen is left adhering to a separate support.

## Reflection Method

With the reflection method the brighter portion of the field consists of totally reflected light, the weaker portion of ordinarily reflected light. With thicker specimens the contrast is ordinarily sufficient; but with thin films the contrast is often so weak that a laborious search is necessary to locate the desired boundary. In such an event there are several ways of increasing the contrast. The common way is to vary the area of the illumination and the angle at which the light strikes the front prism. As a source of diffuse light the writer uses an area about 5 cm. (2 inches) square illuminated by a 15-watt 110-volt bulb. With this source and with the conventional design of Abbe refractometer, which has a horizontal axis about which the whole working part may be rotated as a unit, it is easy to find the angle where the contrast is a maximum.

A second method is to suppress the internal reflection at the film-air boundary, by increasing the film thickness, or if possible by adding a drop of inert liquid of higher refractive index than the film and closing the back prism. This cuts down the stray light which otherwise increases the intensity of the ordinarily reflected portion of the field at the expense of the contrast. This method is useful at times, but it is not always possible (as when a film to be measured is left adhering to a separate support) or convenient.

The third method to increase the contrast makes use of polarized light. A polarizing screen is placed between the front prism and the source with vibration direction at 45° to the plane of incidence, and a cap analyzer over the eyepiece is crossed with it. With these crossed diagonal polarizers, if the film is thin enough and the angle of illumination is correct, a reversal of the fields is almost always noted—there is fairly complete extinction of the totally reflected portion of the field, and a less complete extinction of the ordinarily reflected portion. When the contrast is thus enhanced, the boundary is readily apparent in those cases where it is difficult if not impossible to locate by other methods. The effect is often striking.

Since one would expect the relative intensities of the two portions of the field to be unaffected by the polarizers, the reversal of the fields is at first sight paradoxical. But when it is considered that the stray light resulting from internal reflection at the film-air boundary is the cause of the trouble, the interpretation becomes clearer. When the diagonal polarizer is used, this stray light becomes depolarized in passing through the film, so that it can no longer be extinguished by the analyzer. This depolarization is not, in general, a phase



shift at internal reflection, since the intensity of the portion of the field in question is not found to be reduced appreciably when a quarter-wave plate is inserted in various azimuths and the analyzer is rotated. It is observed, as would be expected, that the reversal of the fields is more distinct when the film is birefringent than when it is optically isotropic; but qualitatively there is little difference between films of weak and of stronger birefringence.

The polarizing method is of considerable practical advantage in a laboratory where refractive index measurements are made on a large number of thin films and the time element is important.

A Polaroid microscope cap analyzer, such as the one listed by the Bausch & Lomb Optical Company and which fits over eyepieces up to 27 mm. in diameter, has been found to be suitable for

the purpose described. Such an analyzer is, of course, a necessity in identifying the double boundaries observed when birefringent films or crystals are examined on an Abbe or other total reflection refractometer (4). Bellingham and Stanley (London) are now offering an Abbe refractometer with polarizing eyepiece (2). The polarizing screen for the illuminator may be obtained from the Polaroid Corporation or other dealers. The combination of polarizing screen and cap analyzer may be used in a simple polariscope for examination of specimens preliminary to their measurement.

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# Effect of Ions on Mohr Method for Chloride Determination

## Hydrogen Peroxide Modification for Sulfite Elimination

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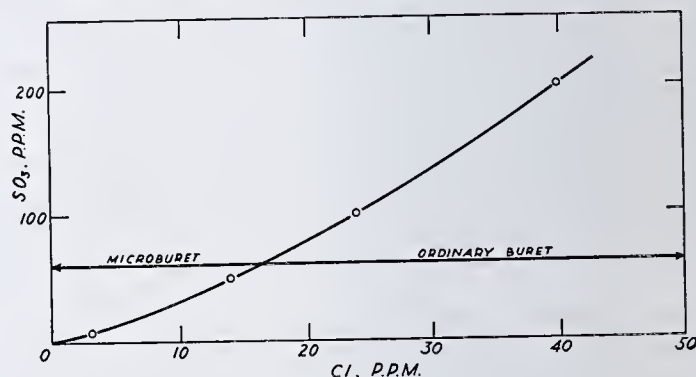
The Mohr method is found to be unaffected by ions, except sulfite, that are prevalent in steam condensate, raw and mixed boiler feed waters, and in boiler salines. A modified Mohr method is suggested for the elimination of sulfite and is proved to be satisfactory. pH between 7.4 and 10.8 has no effect on the method.

THE Mohr method (1) and modifications of it for the determination of chlorides are widely used in boiler feed-water studies and yet a fairly exhaustive search of the literature has failed to disclose complete studies of the effects of the ions prevalent in these waters. Although it was felt that the majority of the ions exert no influence, the present investigation was planned to ascertain just what ions affected the method and to what extent.

Because of the nature of the waters involved in this work, the study of these effects lent itself to subdivision into low and high ranges of chlorides, the former ranging from 0 to 10 p. p. m. and being representative of what would be encountered in steam condensate and in raw and mixed boiler feed waters, and the latter ranging from 10 to 1000 p. p. m. of chloride and representing concentrations encountered in boiler salines. Owing to the absence of adequate samples of various chloride concentrations, synthetic solutions were prepared with known chloride concentration, and the particular ion or ions (chloride-free) to be studied were introduced prior to the titration. Table I presents the results of this work.

Reference to Table I will reveal that the method under these conditions was unaffected in the high chloride range by 3000 p. p. m. of sulfate, 100 p. p. m. of total hardness as calcium carbonate, 400 p. p. m. of silicate expressed as  $\text{SiO}_2$ , 160 p. p. m. of phosphate, 40 p. p. m. of iron (ferric), 2000 p. p. m. of total alkalinity as calcium carbonate, and approximately 10,000 platinum units of color obtained from tannin.

The work showed that sulfite interfered, giving high results. The effect of this ion is also presented in the diagram. In the low range of chloride, ion concentrations of 328 p. p. m. of sulfate, 400 p. p. m. of total alkalinity as calcium carbonate, 600 p. p. m. of total hardness as calcium carbonate, 20 p. p. m. of phosphate, 40 p. p. m. of silicate expressed as  $\text{SiO}_2$ , and 250 platinum units of color were found to have no influence. Sulfite also interfered in this range.



The diagram shows that considerable sulfite is required to give an appreciable interference. This being the case, solutions containing low sulfite and high chlorides will not be seriously affected by the presence of this ion. When, however, the sulfite content is high and the chloride concentration low, the error in the chloride determination can be serious.

To eliminate the effects of sulfite, the following procedure was found to be satisfactory:

After neutralization of the sample to pH 4.3 (methyl orange end point), 2 cc. of hydrogen peroxide (3 per cent by volume) are introduced. The solution is stirred and reneutralized to the alkaline side of methyl orange. This reneutralization step is necessary because the sulfuric acid present in the hydrogen peroxide reduced the pH value, giving slightly high results due to the fugitive nature of the end point. The solution is then ready for titration with silver nitrate after the addition of the chromate indicator. The results using this procedure are presented in Table II.



TABLE I. EFFECTS OF IONS IN CHLORIDE DETERMINATION

Expt.	Chloride			Ions Present							
	Introduced	Found by	Variation	SO <sub>4</sub>	Total H	Total	SO <sub>3</sub> <sup>a</sup>	PO <sub>4</sub>	SiO <sub>2</sub>	Fe	Color <sup>b</sup>
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
High Range of Chloride <sup>c</sup>											
1	400	400	0	...	...	...	...	...	...	...	...
2	1000	998	-2	...	...	...	...	...	...	...	...
3	400	400	0	3280	120	...	...	...	400	...	10,000
4	100	98	-2	...	...	...	...	...	...	...	...
5	400	400	0	...	...	...	...	160	...	...	...
6	400	412	+12	...	...	...	48	...	...	...	...
7	400	400	0	...	...	2000	...	160	40	...	...
8	400	402	+2	...	...	...	...	...	...	40	...
9	400	440	+40	...	...	...	200	...	...	...	...
10	400	424	+24	...	...	...	100	...	...	...	...
11	400	414	+14	...	...	...	50	...	...	...	...
Low Range of Chloride <sup>d</sup>											
1	10	10.6	+0.6	...	...	...	...	...	20	...	...
2	10	9.6	-0.4	328	...	400	...	...	40	40	500
3	10	15.2	+5.2	328	600	...	...	...	40	...	250
4	10	10	0	328	600	...	...	...	...	40	...
5	0	0.6	+0.6	...	...	...	...	...	...	...	...
6	0	0.2	+0.2	...	...	...	...	20	...	...	...
7	0	3	+3	...	...	...	10	...	...	...	...
8	1	1.4	+0.4	...	...	...	...	...	...	...	...
9	5	4.2	-0.8	...	...	...	...	...	...	...	...
10	10	13	+3	...	...	...	10	...	...	...	...

<sup>a</sup> Solid sodium sulfite introduced into titration system immediately before titration. 1000 to 10,000 p. p. m. of mannitol used to preserve SO<sub>3</sub> during analysis.  
<sup>b</sup> Expressed in platinum units of color.  
<sup>c</sup> Conditions for high range: Silver nitrate 1 cc. = 1 mg. Cl<sup>-</sup>. Ordinary buret. 25-cc. sample neutralized to methyl orange end point. 0.2 cc. of 10% neutral potassium chromate. 0.1-cc. blank.  
<sup>d</sup> Conditions for low range: Same as for high range except for microburet. 50-cc. sample. 0.22-cc. blank.

TABLE II. COMPARATIVE RESULTS OF PRECIPITATION, MOHR, AND MODIFIED MOHR METHODS

Expt.	Chloride			SO <sub>3</sub> Present <sup>b</sup> <i>P. p. m.</i>	Type of Sample
	Precipitation method <sup>a</sup>	Regular Mohr method	H <sub>2</sub> O <sub>2</sub> modified method		
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>		
1	97.9	122	100	96	Boiler
2	252	278	254	150 <sup>c</sup>	Boiler
3	125	140	124	50	Boiler
4	7.4	8.7	6.6	5	Raw
5	13.2	15.5	12.6	7	Raw

<sup>a</sup> Precipitation as AgCl.  
<sup>b</sup> Sodium sulfite introduced directly before analysis of samples. 1000 to 10,000 p. p. m. of mannitol used to preserve SO<sub>3</sub> during analysis.  
<sup>c</sup> Approximate.

Table II shows that the hydrogen peroxide procedure for sulfite elimination gives good results when compared to the precipitation method as silver chloride. The regular Mohr method gave high results because the sulfite was not eliminated. The results under the modified method were of acceptable accuracy. Each of these experiments except No. 2 fits very well the curve presented in the figure. The sodium sulfite introduced in experiment 2 was only approximate. Table III presents the composition of the solution used in Table II.

TABLE III. COMPOSITION OF SOLUTIONS USED IN TABLE II

Experiment	1	2	3	4	5
Suspended matter	Present	Absent	Absent	Absent	Absent
Total hardness <sup>a</sup>	0	0	0	104	32
CO <sub>3</sub> <sup>a</sup>	60	184	152	..	..
OH <sup>a</sup>	90	..	..	36	20
HCO <sub>3</sub> <sup>a</sup>	..	36	16	68	16
SO <sub>4</sub>	60	400	688	0	0
Fe	..	0	0	0	0
pH	11.1	10.1	10.1	7.3	6.9

<sup>a</sup> Expressed as calcium carbonate.

During the course of this study, the effect of pH on this determination was investigated. Inasmuch as the chromate indicator buffers the solution all pH measurements were carried out (electrometrically) after the addition of the indicator. The results are presented in Table IV, which shows that the same results were obtained when the titration was performed in any part of the pH range of 7.4 to 10.8. Experiments on solutions above pH 10.8 and below pH 7.4 gave unsatisfactory results, especially in the low range of chloride.

TABLE IV. EFFECT OF pH ON MOHR METHOD

Expt.	Chloride			pH of Solution
	Present <i>P. p. m.</i>	Found <i>P. p. m.</i>	Variation <i>P. p. m.</i>	
1	400	398	-2	11.1
2	400	402	+2	10.5
3	400	400	0	9.9
4	400	400	0	7.7
5	400	402	+2	6.4
6 <sup>a</sup>	400	..	..	5.4
7 <sup>a</sup>	400	..	..	2.9
8	5.3	16.6	+11.3	11.3
9	5.3	5.4	+0.1	10.8
10	5.3	5.2	-0.1	10.6
11	5.3	5.1	-0.2	8.8
12	5.3	5.0	-0.3	7.7
13	5.3	5.6	+0.3	7.4
14	5.3	6.2	+0.9	7.0
15	5.3	8.4	+3.1	7.0
16	5.3	3.2	-2.1	7.0
17 <sup>a</sup>	5.3	..	..	5.6

<sup>a</sup> No end point obtained.

The color reactions of these titrations throughout this pH range of 7.4 to 10.8 were the same, slightly better end points being obtained in the higher pH region. Laboratories which determine chlorides after the analysis of alkalinity titrated to the methyl orange end point incur no error by this procedure, because the chromate buffers this solution from pH 4.3 to 7.7, which is within the acceptable range.

Conclusion

The Mohr method for chloride determination is affected by the presence of sulfite and unaffected by sulfate, total alkalinity, total hardness, phosphate, silicate, iron, and color in quantities that are prevalent in these types of water. The hydrogen peroxide modification of this method suggested for sulfite elimination was found very satisfactory. pH between 7.4 and 10.8 was not found to affect the method.

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# Nitromethane

## Potential Hazards in Use

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IN VIEW of the usefulness of nitromethane in certain laboratory operations, the authors have carried out a number of tests to ascertain the conditions under which it might explode. In view of the results, which indicate that precautions should be taken against subjecting nitromethane to severe shock or to high temperatures and pressures, it appeared advisable to call the matter to the attention of others who may be manufacturing or using this compound.

The explosiveness of nitromethane has been suspected by various investigators, but no demonstration of it has been published heretofore. Although nitromethane cannot be exploded by impact (4), its sodium and ammonium salts are known to be very sensitive, exploding on slight jarring or moderate heating (2), and the polynitromethanes are listed in tests on explosives. On the other hand, nitroethane is reported not to detonate at 96° C. with a No. 8 electric cap (4). Usually no special precautions are taken in the making and handling of the mononitroparaffins in the laboratory (3, 4) or commercially (10) and their shipment comes under no special ban.

### Material

The nitromethane was prepared by the method described in "Organic Syntheses" (1) and its properties are compared below with those given for nitromethane in the International Critical Tables:

	Material Used	Literature Values	Refer- ence
Specific gravity	1.1369 <sup>20</sup> / <sub>4</sub>	1.1354 <sup>21.5</sup> / <sub>4</sub> 1.139 <sup>20</sup> / <sub>4</sub>	8 5
Refractive index	1.3817 <sup>D</sup> / <sub>20</sub>	1.38133 <sup>21.5</sup> / <sub>4</sub> 1.3821 <sup>20</sup> / <sub>4</sub>	8 6
Boiling point (760)	101.4–101.5° C. (uncorrected)	101.1° C. 101.9° C.	7 5

### Detonation and Heat Tests

The tests applied were not those standard for the examination of explosives; rather, they were devised to show conditions under which nitromethane becomes explosive, in order to furnish some idea of its potential hazard in comparison with other materials of more or less similar chemical structure. The experiments, which are described below, show that nitromethane is only moderately sensitive to explosion by detonation or by heat and pressure. When it does explode, however, it does so with a force that qualifies it to be called a very powerful explosive.

The detonation tests on pure and diluted nitromethane and on other materials for comparison were made at about 20° C. The sample, of about 7 ml. contained in a small vial, was placed, along with the detonator, in the cylindrical chamber (diameter 1.9 cm., 0.75 inch) of a steel block 12.5 cm. (5 inches) high by 6.9 cm. (2.75 inches) in diameter that rested on a steel plate and was covered with a 2.27-kg. (5-pound) weight. The height to which this weight was thrown by the explosion gave an approximate measure of the explosive power of the material tested.

The results with a No. 6 fulminate cap are given in Table I. It was also found that pure nitromethane could be exploded with the detonating fuses Cordeau, which is trinitrotoluene in a lead tube, and Primacord, which is pentaerythritol tetranitrate spun into textiles.

Tests on the response of nitromethane and other materials to heat and pressure were made on samples of about 15 mg., sealed in capillary tubes 5 cm. long and about 1.5 mm. in inside diameter with walls about 2.0 mm. thick, which were dropped into a hole drilled in a copper block heated to the required temperature with a Bunsen burner. The results of these heat tests are assembled in Table II.

Table I shows that, though nitromethane is much less sensitive to shock than 40 per cent gelatin dynamite, even a 10 per cent solution of it in methyl Cellosolve is more sensitive

TABLE I. RESPONSE OF NITROMETHANE AND OTHER COMPOUNDS TO SHOCK BY NO. 6 CAP<sup>a</sup>

Compound Tested	Diluent	Distance from Butt of Cap to Sample Inches	Re- sponse	Remarks
A				
Nitrobenzene, 100%	None	0	None	
Nitromethane, 100%	None	0	Explodes	Force considerably greater than 40% gelatin dynamite
		0.5	Explodes	3 out of 3 trials
		0.625	None	3 out of 3 trials
40% gelatin dynamite	None	5.125	Explodes	3 out of 3 trials
		5.25	Explodes	2 out of 3 trials
		5.5	None	3 out of 3 trials
B				
Nitromethane, 25%	Methyl Cellosolve, 75%	0	Explodes	
Nitromethane, 10%	Methyl Cellosolve, 90%	0	Explodes	
None	Methyl Cellosolve, 100%	0	None	
C				
Nitromethane, 98%	Lubricating oil extract, 2% <sup>b</sup>	0	Explodes	
		0.125	None	
Nitromethane, 93%	Coking distillate, 7% <sup>c</sup>	0	Explodes	
		0.125	None	
Nitromethane, 80%	Benzene, 20%	0	Explodes	
		0.125	None	
D				
Nitromethane, 20%	Coking distillate, 80%	0	None	
Nitromethane, 16%	Lubricating oil extract, 84%	0	None	
Nitromethane, 10%	Lubricating oil extract, 90%	0	None	
Nitromethane, 10%	Coking distillate, 90%	0	None	

<sup>a</sup> Cap made by the California Cap Co.

<sup>b</sup> An aromatic furfural extract of a light lubricating oil.

<sup>c</sup> A highly aromatic cracked oil, 30% boiling in the gasoline range.



TABLE II. RESPONSE OF NITROMETHANE AND OTHER COMPOUNDS TO HEAT

Compound Tested	Diluent	Approximate Temperature of Explosion ° C.	Remarks
A			
Nitromethane, 100%	None	410	Immediate
Nitrobenzene, 100%	None	410	After a few minutes
Nitroethane, 100%	None	450	After a few minutes
Nitroglycerine, 100%	None	200(9)	Immediate
B			
Nitromethane, 75%	Methyl Cellosolve, 25%	460	Immediate
Nitromethane, 50%	Methyl Cellosolve, 50%	460	Immediate
Nitrobenzene, 50%	Methyl Cellosolve, 50%	495	Immediate
Nitromethane, 20%	Coking distillate, 80%	490	Immediate
C			
Nitromethane, <20%	Coking distillate, >80%	...	No explosion at 500° C. for 15 minutes
None	Water, 100%	...	No explosion at 500° C. for 15 minutes
None	Methyl alcohol, 100%	...	
None	sec-Butyl alcohol, 100%	...	
None	Methyl cyanide, 100%	...	
None	Ethyl cyanide, 100%	...	

than pure nitrobenzene. Methyl Cellosolve, though not explosive itself, forms explosive mixtures with even small proportions of nitromethane. Solutions of aromatic hydrocarbons in nitromethane are, as part C of Table I shows, explosive, though much less sensitive than pure nitromethane. Solutions of nitromethane in aromatic hydrocarbons, at least up to 20 per cent concentration, appear to be safe (part D).

As part A of Table II shows, nitromethane is not much more sensitive to heat than nitrobenzene, a temperature of 410° C. detonating both of them, the nitrobenzene after a short delay. Dilution of the two compounds with equal volumes of methyl Cellosolve shows that the nitrobenzene mixture is less sensitive than the one containing nitromethane, requiring a temperature of 495° C. instead of 450° C.

Conclusion

From the foregoing results, it is concluded that because of the risk of explosion, nitromethane should not be used without due precaution, particularly under conditions of elevated temperature and pressure.

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# Iron Determination in Presence of Titanium

## Using Zinc Reduction

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IN THE oxidimetric titration of iron, the use of amalgamated zinc for reduction of the iron is not only convenient, but, as indicated by Hillebrand and Lundell (2), leads to more accurate results than some other reductants when such interfering substances as titanium, chromium, columbium, molybdenum, uranium, tungsten, vanadium, arsenic, nitrates, and organic matter are absent. The presence of considerable amounts of these interfering substances can usually be apprehended by the formation of a colored solution during reduction. Titanium, in particular, is easily recognized, since the presence of slightly more than 0.1 mg. gives a distinct violet color to the reduced solution.

Vanadium, however, must be present to the extent of 4 to 5 mg. before the color (lavender on leaving the reductor, owing to divalent vanadium, but changing quickly to the green and blue tri- and tetravalent forms, respectively, on exposure to the air) is easily observed. The usual smaller amounts (less than 1.0 mg.) are easily detected by applying the strychnine sulfate test to a few drops of the solution after permanganate titration. Vanadium is also reduced by the other common reductants including hydrogen sulfide, and when present in appreciable amounts necessitates a special procedure in the determination of iron. In the presence of permanganate in acid solution, vanadium is oxidized to the pentavalent form, but aeration is not effective in promoting this complete transformation, or transformation to a definite stage so as to allow an accurate correction in the iron titration.

In the analysis of highly siliceous rocks and clays, vanadium is seldom present in sufficient amounts to cause a serious error in the iron titration.

Fortunately, of the substances interfering in the titration of iron after zinc reduction, only titanium is apt to be present in appreciable amounts in the ordinary run of soil and rock analysis; hence if the interference of titanium could be prevented, the desirable zinc reduction method could be used for the determination of iron in many additional cases. In an attempt to accomplish this, Gooch and Newton (1) developed a procedure in which bismuth oxide, cupric oxide, or cupric sulfate is added to reoxidize the titanium selectively. After filtration from the excess of oxidizing agent and reduced product formed, the iron solution is titrated with standard permanganate. Recently, Thornton and Roseman (3) attained the same result by simply bubbling air through the reduced solution for 10 to 30 minutes, so as to reoxidize the titanium but leave the iron unaffected. The writers found that this procedure gives good results when small amounts of titanium are present, but is somewhat slow with larger quantities.

Reoxidation of Titanium

Prior to a knowledge of Thornton and Roseman's work, the writers had found it possible to reoxidize the titanium selectively by stirring or shaking the solution containing the iron and titanium in reduced form. After making a number



TABLE I. STABILITY OF FERROUS SULFATE IN ACID SOLUTION TO OXIDATION BY AERATION WITH ATMOSPHERIC OXYGEN

How Aerated	Recovery of Iron by Titration after Aeration		10 Minutes		30 Minutes		2 Hours	
	Mg.	%	Mg.	%	Mg.	%	Mg.	%
Aerated water added and stirred	25.40	100.0	25.40	100.0	...	...	...	...
Stirred	25.40	100.0	25.40	100.0	...	...	...	...
Aspirated	25.40	100.0	25.40	100.0	25.37	99.9	...	...
Shaken	25.40	100.0	...	...	25.45	100.2	...	...

of tests, the following procedure was found to be effective, rapid, and convenient:

If, after passage of the solution through a Jones reductor, a violet color in the solution is not observed on examination against a white background, it may be concluded that less than 0.1 mg. of titanium is present, and this amount is quantitatively oxidized by stirring the solution vigorously for 3 minutes in a 400- or 600-cc. beaker. If, on the other hand, a violet color is observed, 0.1 mg. or more of titanium is present, and this is quantitatively oxidized by adding 50 cc. of distilled water (this water should be in equilibrium with the air, so as to contain considerable dissolved oxygen) to the solution and stirring vigorously for at least 3 minutes after the last trace of violet color has disappeared. In either case it may now be assumed that the titanium present has been completely oxidized. The total volume of the solution should be kept as small as is possible, usually 200 to 250 cc., since stirring has been found to be more effective the smaller the total volume of solution.

### Efficiency of Aeration Procedures

The efficiency of aeration by stirring, shaking, and aspiration for the oxidation of titanium is shown in Figure 1. Solutions of titanium sulfate containing 5 per cent of sulfuric acid by volume were passed through a Jones reductor to reduce the titanium, and the reduced solutions were collected in an atmosphere of carbon dioxide to prevent oxidation before the aeration treatments were begun. Both shaking and aspiration were carried out in the same flasks in which the solutions

per cent of sulfuric acid by volume is given in Table I. After the desired treatments, the iron was titrated with 0.5 *N* permanganate solution. None of the aeration treatments caused a measurable oxidation of the iron when continued for a period of 30 minutes. Even the influence of the 2-hour period is hardly noticeable.

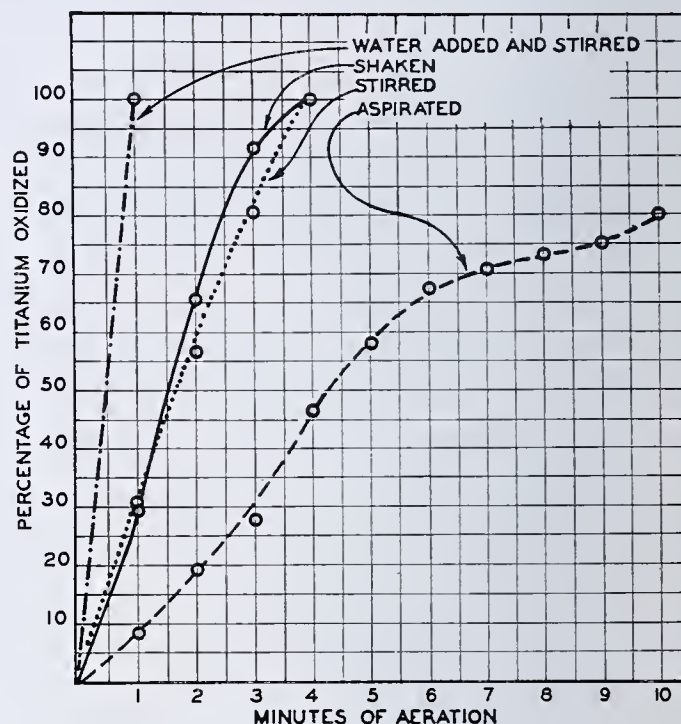


FIGURE 1. AERATION EFFICIENCY

In order to test the selective oxidation of titanium by aeration in the presence of iron, and the accuracy of the iron titration thereafter, solutions containing 25.4 mg. of iron, 11.8 mg. of titanium, and 5 per cent of sulfuric acid were passed through a Jones reductor and then titrated with 0.5 *N* permanganate solution after various aeration treatments. The results are given in Table II. Aeration effected by the addition of water followed by stirring for 2 minutes resulted in complete recovery of the iron without interference due to titanium. To obtain the same result by stirring without adding water required 7 minutes of stirring. Similarly, aspiration required 10 minutes.

TABLE II. RECOVERY OF IRON

(From solutions containing 25.40 mg. of iron and 11.8 mg. of titanium by titration after reduction with amalgamated zinc using the Jones reductor and aeration to reoxidize titanium)

How Aerated	Apparent Recovery of Iron after Aeration Periods Indicated													
	1 Minute		2 Minutes		3 Minutes		6 Minutes		7 Minutes		10 Minutes			
	Mg.	%	Mg.	%	Mg.	%	Mg.	%	Mg.	%	Mg.	%		
Aerated water added and stirred	26.05	102.6	25.40	100.0	...	...	29.10	114.5	25.60	100.6	25.40	100.0	...	...
Stirred	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Aspirated	...	...	...	...	...	...	26.20	103.1	...	...	25.42	100.2	...	...

were collected from the reductor, so as to prevent agitation before the treatments were begun. Solutions to be stirred were carefully poured into a beaker, and the receiving flask was rinsed with boiled distilled water in an effort to retain all the titanium in the reduced state until stirring could be started. After the desired treatments, the amount of titanium remaining in the reduced condition was determined by titration with 0.5 *N* potassium permanganate solution.

It is evident from Figure 1 that, of the treatments tested, the addition of distilled water to the reduced solution, followed by stirring, effects the most rapid oxidation of the titanium. In this way 11.8 mg. of titanium were oxidized in 1 minute. Stirring and shaking are of about equal effectiveness, 4 minutes being required in either case for the oxidation of 11.8 mg. of titanium. Oxidation by aspiration is somewhat slower, 20 per cent of the titanium being left in the reduced state after 10 minutes.

The influence of similar aeration treatments on the oxidation of similarly reduced iron sulfate solutions containing 5

### Summary

In agreement with the results of previous workers, it was found that interference by titanium in the oxidimetric titration procedure for iron involving the use of amalgamated zinc for reduction can easily be eliminated by aeration immediately after reduction, so as to reoxidize the titanium selectively. This selective oxidation by aeration after passage of the solution through a Jones reductor is effected more conveniently and expeditiously by adding a little aerated water and stirring for a few minutes than by aspiration.

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# Determination of Germanium in Minerals and Solutions

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OF THE numerous elements which are detrimental to the electrolysis of zinc, germanium is the most elusive and one of the most troublesome. Its noxious effect was pointed out in 1930 by Tainton (9), who stated that 0.1 mg. per liter of electrolyte produces noticeable reduction of current efficiency. In zinc plants where cyclic leaching is used germanium is partially precipitated in the neutral leach, but this precipitate is partly dissolved in the acid leach. Thus a considerable load of germanium accumulates before equilibrium is reached, when the solution may contain several milligrams per liter of the element. Members of the metallurgical staff of the Anaconda Copper Mining Co. (2) stated in 1920: "the zinc deposit was nearly ideal, until the first of December when it began to show signs of surface corrosion. The character of the deposit gradually changed until its resemblance to the arsenic deposit in the test cell could no longer be mistaken; but the chemists reported no arsenic in solution." Undoubtedly the source of the trouble was germanium.

The single potential of  $\text{Zn}$ ,  $\text{Zn}^{++}$  is given by Lewis (4) and associates as 0.7581. The electrolysis of zinc from acid solution is possible only because zinc has a high hydrogen overvoltage, and the noxious effects of impurities are due to their lowering the hydrogen overvoltage. The injurious impurities are in two distinct regions in the periodic table: The eighth group metals—namely, iron, cobalt, nickel, and the platinum metals—along with the 1B family occupy one region. The other includes metalloids which form gaseous hydrides—namely, arsenic, antimony, tin, germanium, selenium, and tellurium. In zinc electrolysis the impurities which may be present are iron, cobalt, nickel, copper, germanium, arsenic, and antimony. There are sensitive chemical tests for all these elements except germanium. For this reason at least one large zinc plant has installed a quartz spectrograph.

In 1928 one of the authors was confronted by the problem of eliminating germanium from solutions and was handicapped by lack of a qualitative test for that element, capable of detecting 0.1 mg. or less. A frequently employed method, precipitation of white germanium sulfide and confirmation as potassium fluogermanate, sparingly soluble in hydrofluoric acid solution, is incapable of detecting much less than 1 mg. of germanium. While analyzing minerals by the methods of Noyes and Bray (8), the lack of sensitivity of the sulfide-fluogermanate test again became evident. The methods presented in this paper, developed from research undertaken by the writers to improve on previous methods of germanium analysis, comprise the following features:

Treatment of solids with hydrofluoric, nitric, and sulfuric acids and subsequent extraction with sodium sulfide.

Use of metallic copper to precipitate arsenic and antimony.

Fractional distillation with hydrochloric acid, thus reducing the volume of the distillate to 10 per cent of the original volume.

A modification of the Marsh test for traces of germanium which is capable of detecting 0.001 mg.

A gravimetric method for larger amounts by evaporating the hydrochloric acid distillate with hydrofluoric, sulfuric, and perchloric acids which gives germanium dioxide directly without precipitation by hydrogen sulfide and subsequent ignition.

When bringing minerals into solution, the use of hydrofluoric acid cannot be avoided. Silica holds up germanium, as noted by Lundin (5) and verified by the authors, involving possible loss of germanium as germanium fluoride. The subsequent

removal of excess hydrofluoric acid by evaporation with perchloric or sulfuric acid may lead to another loss of germanium, apparently through the formation of the insoluble form of germanium dioxide described by Müller and Blank (6) and confirmed by Laubengayer and Morton (3). Experiments showed that the former loss occurred when  $\text{GeF}_6$  was too rapidly decomposed; the latter while strong acids were being heated to fuming. Thus we seem to be confronted by a dilemma. If the acids are fumed too rapidly, germanium seems to be lost as germanium fluoride; if we raise the temperature slowly to avoid this loss, germanium has more opportunity to pass into the insoluble rutile form of the oxide.

The authors have found that the insoluble form dissolves readily in hot dilute alkali if a little sodium sulfide is present. A small crystal of sodium sulfide nonahydrate is sufficient. The thiogermanate ion is not decomposed by a small excess of mineral acid, a fact that permits at this point separation of germanium from any arsenic or antimony which may be present.

Most methods proposed for the separation of germanium from arsenic and antimony are based upon distillation of germanium chloride with hydrochloric acid and simultaneous oxidation of the arsenic and antimony to nonvolatile compounds.

The authors have found that the presence of finely divided copper in the distillation flask precipitates arsenic and antimony. It is common practice in the electrolytic zinc industry to add copper sulfate to solutions before purifying with zinc dust. The precipitated copper has a specific effect on the removal of arsenic and antimony from solution, which is probably due to the formation of arsenides and antimonides of copper. This led the authors to try the effect of copper on arsenic and antimony in strong hydrochloric acid solutions.

Several grams of chopped copper foil were added to 50 ml. of hydrochloric acid containing 100 mg. of arsenic trioxide. The copper was immediately blackened. After standing for 15 minutes the copper and acid were distilled together, and the distillate was made 6 *N* in acid and saturated with hydrogen sulfide. No arsenic sulfide was visible.

The above test was repeated using 100 mg. of antimony trioxide in place of arsenic trioxide. Antimony behaves like arsenic.

Fifty milligrams of germanium dioxide, 100 mg. of arsenic trioxide, and 100 mg. of antimony trioxide were distilled in the apparatus shown in Figure 1. On saturation of the distillate with hydrogen sulfide characteristic white germanium sulfide precipitated. The recovery was 98 per cent.

Subsequent work showed that the precipitation of arsenic with copper foil is not complete enough to give a blank Marsh test. Precipitated copper, which is much more reactive because of its finely divided state, was therefore substituted. When much arsenic is present, a preliminary precipitation before distillation removes all except traces which are precipitated in the subsequent distillation in the presence of copper.

In the authors' first experiments on distillation, refluxing was employed solely to prolong the action of copper. Although it was expected that germanium chloride would return to the flask, all the germanium escaped from the condenser. Lundin (5, p. 152) has noted that germanium chloride is very difficult to condense and that correct concentration of hydrochloric acid is important, and advises a concentration



slightly less than the constant-boiling mixture in order to condense all vapors passing into the condenser. It occurred to the authors that by using a concentration somewhat greater than constant-boiling and refluxing, germanium chloride and hydrogen chloride would pass out of the condenser; if water absorbed these vapors completely, the germanium could be collected into a small volume. The passage of air bubbles through the apparatus at the beginning of distillation caused a slight loss, which was avoided by sweeping all the air out of the apparatus with hydrogen chloride before introducing the germanium-containing solution.

Oxidation during distillation involves either passing chlorine through the solution being distilled, or adding potassium permanganate or other reagents which generate chlorine. Loss of germanium seems to be inevitable whenever insoluble gases are allowed to bubble through the receiving liquid. This raises an objection to the use of oxidants in the distillation and constitutes a valid argument for the use of copper which also reduces the decided tendency to bump during distillation.

Comparison of Marsh tube deposits of more than 0.1 mg. is inaccurate. Gravimetric determination is facilitated and precipitation as germanium sulfide avoided by taking advantage of the stability of the fluogermanate ion. When hydrogen chloride-germanium chloride solution is slowly evaporated with hydrofluoric acid in presence of both perchloric and sulfuric acids, no germanium is volatilized. With hydrofluoric and perchloric acids, three experiments gave 97 per cent recovery. With hydrofluoric and sulfuric acids three experiments gave 99 per cent recovery. When both perchloric and sulfuric acids were used, two experiments gave 100 per cent recovery. Why the two latter acids used together are more effective in retaining germanium is not obvious; presumably the relative stability of  $\text{GeCl}_6^{--}$  and  $\text{GeF}_6^{--}$  is involved. Possibly at the lower fuming temperature of perchloric acid  $\text{GeF}_6^{--}$  is not entirely decomposed and germanium fluoride is lost during the subsequent ignition to the oxide. When sulfuric acid is used the rise in temperature is more rapid and germanium chloride may escape if the conversion of  $\text{GeCl}_6^{--}$  to  $\text{GeF}_6^{--}$  has not yet been completed.

Müller and Smith (7) studied the application of the Marsh test to germanium and reported on the effectiveness of various hydrogen generators, concluding that a 2 per cent sodium amalgam gives the best results and that zinc and hydrochloric acid are not satisfactory. Since the latter is the generator most convenient when the germanium has been collected in a small volume of hydrochloric acid solution, the authors thoroughly investigated it. Results of many experiments showed that as little as 0.001 mg. could be detected, but only when the following conditions were exactly maintained:

1. The zinc must be in finely divided flaky form and previously proved to be absolutely free from arsenic and germanium. Not all electrolytic zinc is sufficiently pure. The preparation of satisfactory zinc is described below.
2. Concentrated and not dilute hydrochloric acid must be used. The germanium must be in fairly concentrated hydrochloric acid and must fall in drops directly upon the zinc.
3. The germanium must have been separated from all contaminating elements by previous distillation.

Müller and Smith (7, p. 1910) when using zinc and acid observed the formation of a brown solid which they thought either a form of elementary germanium or a lower hydride. Bardet and Tchakirian (1) observed the same substance but thought it germanium monoxide, stating that with zinc and 25 per cent sulfuric acid they were able to detect 0.1 mg. of germanium by this precipitate. The authors investigated its formation as a test for germanium. In 15 ml. of acid

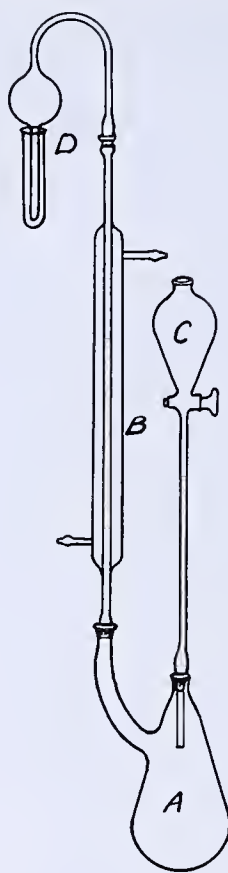


FIGURE 1. DISTILLATION APPARATUS

- A. 300-ml. Erlenmeyer flask  
B. Pyrex condenser, 30 cm. long  
C. Dropping funnel  
D. Delivery tube with safety bulb and test tube

0.1 mg. of germanium gave a distinct precipitate; 0.01 mg. occasionally but not consistently gave a precipitate. The substance seemed to form most readily in 4 to 6 *N* hydrochloric acid on addition of a piece of zinc. It forms at the surface of the zinc but at once detaches itself, leaving no stain on the zinc. It has a greasy appearance and creeps up the wall of the tube. Its formation interferes with the generation of germane. Under the conditions laid down in 2 it is not formed, all the germanium being converted into germanium hydride.

By comparison with deposits from known amounts of germanium, the Marsh test is sufficiently quantitative for 0.1 to 0.001 mg. A portion of the hydrogen chloride-germanium chloride distillate containing not more than 0.1 mg. should be taken, as more than 0.1 mg. makes too dense a deposit for accurate comparison. When several milligrams are present gravimetric determination is advisable.

## Recommended Methods

**A. EXTRACTION OF GERMANIUM FROM MINERALS.** Treat 1 gram of the finely ground material with 10 ml. of nitric acid, 10 ml. of hydrofluoric acid, and 2 ml. of sulfuric acid (1 to 1) in platinum. Moisten sulfide ores with a few drops of water, add the nitric acid gradually until the evolution of nitric oxide has ceased, then add the other acids. Evaporate at low heat, not allowing to boil. Ascertain the absence of hydrofluoric acid by holding a strip of moistened filter paper over the vessel. When white fumes cease to form, the heating has been sufficient. The sulfuric acid should not fume.

Wash the contents of the platinum dish into a small beaker. Make basic with 6 *N* sodium hydroxide, add a crystal (about 0.5 gram) of sodium sulfide nonahydrate, and boil 15 minutes. Cool, make just acid with sulfuric acid (1 to 1), and allow to stand until the sulfur has coagulated, preferably overnight. Filter and wash once with a little water.

Add 1.5 volumes of concentrated hydrochloric acid to 1 volume of the solution and 2 to 3 grams of the copper reagent. Treat further as under C.

**B. TREATMENT OF SOLUTIONS.** To a volume of solution expected to contain 0.001 to 0.1 mg. of germanium add 1.5 volumes of concentrated hydrochloric acid and 2 to 3 grams of the copper reagent. Allow to stand for 1 hour. If the copper is noticeably blackened (arsenic, antimony), filter through an acid-hardened paper, add more of the copper, and allow to stand 15 minutes longer. Then distill as described under C.

**C. DISTILLATION.** Use an apparatus with ground-glass joints similar to that shown in Figure 1. A is a 300-ml. Erlenmeyer flask with the bottom blown out round. The stem of the dropping funnel should be at least 25 cm. (10 inches) long to overcome back pressure. The gooseneck attached to the Liebig condenser should have a safety bulb about 5 cm. (2 inches) in diameter.

Transfer the hydrochloric acid solution obtained in A or B to the flask, washing in the copper with hydrochloric acid (1.5 to 1). Before starting the distillation rinse the condenser and delivery tube with concentrated hydrochloric acid to prevent hydrolysis of germanium chloride, place the test tube containing 5 ml. of water in a beaker of ice water, and adjust the delivery tube to extend almost to the bottom. Start the condenser water and heat the contents of the flask slowly to boiling. Continue the distillation until the water in the receiving tube is saturated with hydro-



hydrochloric acid. If the evolution of hydrogen chloride gas becomes too slow, because the acid in the flask approaches constant-boiling composition, add concentrated acid dropwise through the funnel. To saturate the water in the receiver should require about 0.5 hour.

**D. GRAVIMETRIC DETERMINATION.** The usual method of precipitation as germanium sulfide and conversion to germanium dioxide can be applied. Since the volume of the distillate is small, it is more convenient to use the following method:

Add an equal volume of 27 *N* hydrofluoric acid to the distillate in a weighed platinum dish. Then add 1 ml. of concentrated sulfuric acid and 1 ml. of 60 per cent perchloric acid, and evaporate on a steam plate, not permitting to boil. Fume the heavy acids slowly to dryness and ignite. Weigh as germanium dioxide.

**E. MODIFIED MARSH TEST.** A satisfactory apparatus consisted of a 20-cm. (8-inch) test tube as generator, carrying a two-hole rubber stopper through which passed the 25-cm. (10-inch) stem of a small dropping funnel and a delivery tube leading to a gas-washing bottle. (The authors used a scrubber provided with a sintered-glass filter, 10.) The scrubbed gas passed through a straight drying tube loosely stuffed with glass wool, and then to the combustion tube. This consisted of Pyrex 0.6 cm. (0.25 inch) in external diameter and 12.5 cm. (5 inches) long, drawn out to a capillary 5 cm. (2 inches) long and about 1 mm. in internal diameter at the farther end.

Place in the test tube about 5 grams of zinc (free from arsenic and germanium) prepared as described below, and in the dropping funnel 5 ml. of 12 *N* hydrochloric acid, proved free from arsenic and germanium. Before closing the test tube, make sure that the stem of the funnel is filled to assure free dropping of the acid into the tube. Open the cock in the funnel to permit the acid to enter at a rate of about 1 drop per second. Close the cock before air enters the stem and test the emerging hydrogen for quiet burning by igniting a tubeful caught under water. If there is no further danger of explosion, slip the combustion tube in place and heat with a Bunsen burner about 1.8 cm. (0.75 inch) before the constriction. Since the Pyrex is heated to incipient softening, the tube should be supported on both sides of the flame.

Now add the distillate from C and allow it to flow into the generator at a rate of 1 drop per second. When the distillate has nearly all entered the stem, add 5 ml. of pure hydrochloric acid to flush it out. Allow the action to continue for 15 minutes after all the acid has entered the generator.

With pure reagents the stain in the combustion tube is due to germanium. Standard tubes for comparison should be taken through the whole procedure.

This test is quantitative for amounts of germanium between 0.1 and 0.001 mg. If more than 0.1 mg. is present the stain is too heavy to be estimated.

### Accuracy of Methods

**MODIFIED MARSH TEST FOR TRACES.** The authors have repeatedly carried small quantities of germanium, 0.1, 0.01, and 0.001 mg., through this procedure and compared the Marsh tubes with those produced by adding the germanium directly to the Marsh generator. The comparison was good where 0.1 and 0.01 mg. were used. Where only 0.001 mg. was taken through the procedure, the stain in the Marsh tube was somewhat dimmer than that produced by the same amount added directly to the generator. For this reason standard tubes should be taken through the whole procedure.

**GRAVIMETRIC METHOD.** Two tests taking 50 mg. of germanium dioxide through the procedure showed a recovery of 98 per cent.

### Preparation of Special Reagents

**PRECIPITATED COPPER.** Dissolve 100 grams of copper sulfate in 1 liter of water. Precipitate the copper with granulated zinc, using some excess. Then acidify with 18 *N* sulfuric acid to dissolve the excess zinc and boil, adding more acid until the action ceases. The precipitate should be bright red. Decant the acid solution, wash several times with water, transfer to a wide-mouthed bottle, and keep covered with water.

**ARSENIC- AND GERMANIUM-FREE HYDROCHLORIC ACID.** Arsenic-free hydrochloric acid for the Marsh or Gutzeit tests is satisfactory if proved by blank runs.

**REAGENT ZINC.** The zinc must be free from arsenic, antimony, and germanium. Zinc in suitably small flakes was prepared by the following method:

Electrolytic zinc was melted in an assay crucible using ammonium chloride as a flux. When the zinc was well melted and the crucible at a bright red heat, the metal was poured through a 100-ml. Alundum crucible with a 2-mm. hole in the bottom and allowed to fall about 6 meters (20 feet) into a bucket of ice water. The impact of the molten zinc on the water causes it to spatter out into thin flakes. If sufficiently pure zinc is not obtainable, metal of very high purity can be prepared by electrolysis.

Purify 5 liters of zinc sulfate solution containing 100 grams of zinc per liter by the following method: Add sufficient ferric sulfate to give 2 to 3 grams of iron per liter and heat nearly to boiling. Add zinc oxide until the iron is precipitated, then potassium permanganate to permanent pink, boil 15 minutes, and filter. Arsenic, antimony, germanium, and cobalt are removed. To the filtrate add copper sulfate to give a copper content of 1 gram per liter and heat to boiling. Add 5 grams of zinc dust per liter, boil 30 minutes, and filter.

Electrolyze in a 2-liter battery jar or beaker, using an aluminum cathode with edges framed with wood to facilitate stripping the zinc. Use two lead anodes having a submerged area twice that of the cathode. The anodes can be suspended by folds over the edge of the jar. Cathode current density should be about 30 amperes per 0.0992 sq. meter (1 square foot). With a submerged cathode area (both sides) of 154.8 sq. cm. (24 square inches) and a current efficiency of 90 per cent, about 6 grams of zinc per hour are deposited. The quality of the deposit is best when the acidity of the electrolyte is about 90 grams per liter of sulfuric acid. Since sulfuric acid may contain arsenic and other impurities, it is preferable to establish optimum acidity through electrolysis. This acidity will have been reached when about 60 grams of zinc have been deposited per liter of electrolyte—that is, after 20 hours if 2 liters are being electrolyzed. Thereafter, 6 grams of zinc should be added each hour that the cell is run, by withdrawing 100 ml. of the electrolyte and replacing it with 100 ml. of the purified solution. The electrolyte should be titrated occasionally to verify the acidity. The cathode is stripped daily. The deposit is broken up and the flaky form prepared as described above.

### Summary

Germanium can be accurately determined in minerals or solutions by a modified Marsh test when less than 0.1 mg. is present, gravimetrically when larger amounts are involved.

Losses of germanium through volatilization as germanium fluoride and through formation of the acid-insoluble form of germanium dioxide are provided against.

Modifications of the Marsh test permit the detection of 0.001 mg. of germanium, even when using a zinc-hydrochloric acid generator.

The preparation of reagent copper used in the proposed methods and of electrolytic zinc of the high purity essential for the Marsh test for germanium is described.

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RECEIVED June 16, 1937. Abstracted from a thesis submitted by Mr. Aitkenhead to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. A copy of the complete thesis may be borrowed from the Purdue University Library through the Inter-Library loan. The quantitative data upon which statements in this paper are based will be found therein.



# A Standardized Method for the Determination of Vitamin B<sub>1</sub>

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**B**IOLOGICAL assay of vitamin B<sub>1</sub>, wherein the rat is used as the experimental subject, has been based upon rate of growth or the cure of polyneuritic reactions. Chase and Sherman (2) presented detailed data which served to clarify the significance of growth rate as a practical criterion for the determination of vitamin B<sub>1</sub>. Notwithstanding the wide use of this method, with or without minor modifications, the specificity of convulsions, incoördination, and other reactions of a characteristic nature are believed by many to be a more reliable and satisfactory basis for assay purposes. Bender and Supplee (1) have shown that the growth response of the rat is dependent upon small variations in the relative amounts of certain other entities of the vitamin B complex as well as the amount of vitamin B<sub>1</sub>. Even though growth response was shown to be commensurate with the vitamin B<sub>1</sub> intake, the evidence clearly indicated that precise and accurate interpretation of the growth record must presuppose a definite knowledge of the exact and relative amounts of the other water-soluble factors present.

Evidence now available seems to substantiate the belief that irrespective of whether growth or the polyneuritic reaction is used as the criterion for vitamin B<sub>1</sub> assays, further standardization of technique with consequent greater reliability of interpretation of results is possible by using a simplified basal ration supplemented by fixed doses of pure entities or standardized concentrates of such entities, as a means of supplying other dietary prerequisites. The details of a standardized procedure involving these considerations follow. The method is in substance a refinement and simplification of the rat curative method proposed by Smith (3) and further modified by Waterman and Ammerman (5).

## Procedure

**ANIMALS.** White rats from the usual inbred stock colony are weaned to the basal diet and distilled water when 40 to 50 grams in weight. At this laboratory such rats are usually 21 to 23 days of age. The stock ration of the breeding colony consists of ground whole yellow corn, 51 parts; linseed-oil meal, 16 parts; whole milk powder (Roller process), 25 parts; ground alfalfa-leaf meal, 2 parts; XXX water-soluble milk vitamin concentrate—Labco—(60 per cent solids), 8 parts; and calcium carbonate, one-half part. No supplements or modifications of this regimen have been used for a period of about 8 years.

**BASAL DIET AND SUPPLEMENTS.** At the time of weaning, the animals are placed in individual cages with screened bottoms and given the following basal diet, ad lib.:

Vitamin-free casein (Labco)	20 parts
Sucrose	69 parts
Salt mixture No. 40 (4)	4 parts
Powdered agar-agar	2 parts
Hydrogenated vegetable oil (Crisco)	3 parts
Cod liver oil (medicinal grade)	2 parts

At the end of a 2-week period the following additional supplements are provided per rat per day while continuing the basal diet, ad lib.:

10  $\gamma$  of lactoflavin (Labco lactoflavin, riboflavin. PX, 1E, or 2EK grades are suitable)  
0.75  $\gamma$  of pure vitamin B<sub>1</sub> (Merck or equivalent)  
100 mg. of autoclaved rice polish concentrate (Labco)<sup>1</sup>

These supplements are dissolved together in such concentration that 2.5 to 3.5 cc. of an aqueous solution carry the requisite

<sup>1</sup> The rice polish concentrate available in desiccated form is dissolved in water at a 7.5 per cent concentration, the pH value adjusted to 8.5, and the alkaline solution autoclaved 5 hours at 120° C.

amount of each required per rat per day. It is convenient to make up sufficient of this standardized water-soluble vitamin supplement to meet the requirements for a period of one week or more, keeping the mixture in the refrigerator when not being used.

The standardized water-soluble vitamin supplements are fed daily to the individual animal by measuring the required amount of the solution (2.5 to 3.5 cc.) in small easter cups with a suitable pipet calibrated at intervals of 0.1 cc. A double dose may be fed on Saturday to provide for the Sunday requirement. The supplements are consumed promptly by the animals.

## Development and Diagnosis of Polyneuritis

The animals are weighed once a week for the first 4 weeks, then 3 times weekly, and when polyneuritis commences to appear they are weighed daily. The weight of the animals during the first week on the basal diet usually increases very slightly, and there is also a slight stimulus during the first week of the supplement feeding. This latter stimulus causes a weight increase of about 6 to 8 grams, followed by substantially constant weight until the appearance of polyneuritis, when the weight of the animals varies from about 40 to 55 grams.

At the approach of the critical period (about the fifth week after weaning) the animals are examined twice a day for polyneuritis which is characterized by spasticity, tremor, or incoördination. (While the critical period at which the majority of animals in these laboratories begin to show the characteristic symptoms of polyneuritis is about 6 weeks following weaning, this period may vary in other laboratories. It has been found that if certain animals fail to show polyneuritis after an extended period, reduction in the amount of the 0.75  $\gamma$  of pure vitamin B<sub>1</sub> supplement or its complete elimination for a few days will induce the characteristic reaction in many of those animals showing prolonged resistance on the 0.75  $\gamma$  level.)

The animal is stimulated by whirling by the tail for a definite number of revolutions, such as 3 complete turns, or by quickly turning the animal over on its back. In any case uniformity of degree of stimulation should be adopted. Varying degrees or forms of the paralytic reaction are evident, such as (1) spasticity or muscular tenseness with legs stretched out and back hunched up; (2) tremor or twitching of muscles as when legs are partly outstretched with paws vibrating rapidly; or (3) incoördination, as when the animal loses its ability to move in any given direction, moves in circles, or rolls over and over. The degree of severity of the polyneuritis symptoms is indicated as follows:

**ACUTE.** Advanced polyneuritis with prolonged or continuous contractions.

**MEDIUM.** Medium polyneuritis with recovery from symptoms within a very few seconds.

**SLIGHT.** Suggestion of polyneuritis, detectable symptoms with immediate recovery from contractions following stimulation.

## Selection of Animals and Dosage

Only those animals showing at least the medium degree of polyneuritis are used for assay (practically all animals can be selected at this stage if examined twice daily during the critical period). The substance to be assayed is dissolved in water or uniformly suspended in an 0.5 to 1.0 per cent gum tragacanth solution, if insoluble. It is desirable, if possible,



to have the test substances of such concentration that the dose will be carried in 0.10 to 0.25 cc.

The desired dose is accurately measured by means of a glass syringe fitted with a cut-off coarse-gage needle. The dose is administered by introducing the needle of the syringe far back in the throat at the extreme base of the tongue, and slowly forcing the dose from the syringe.

### Determination of Cure

A positive cure is defined as the relief of all the nervous symptoms for a period of at least 4 days, time being counted when the animal appears cured. In testing the dosed rats, care should be used to stimulate them to the same degree as was used for the original diagnosis, examinations being made twice daily. If the treated rat remains paralytic for 48 hours following the test dose, the dose is not considered adequate and the animal is then given a dose of vitamin B<sub>1</sub> standard which has been found adequate to produce the desired cure; such animals are thus conserved for a further test on recurrence of the paralytic reactions. If the dose is marginal and cure uncertain, the animal should not be given the standard vitamin B<sub>1</sub> concentrate dose for at least 96 hours. This procedure determines if an animal is abnormal and also saves it for further assays. In a great majority of instances a single rat may be used for a succession of assays, four to six suitable reactions being of common occurrence, and frequently a sequence of 7 to 10 reactions may be obtained from a single animal.

TABLE I. WEIGHT RANGE OF ANIMALS RECEIVING THE STANDARDIZED BASAL DIET

Weight Range Grams	Per Cent of Animals	
	After 42 days	After 70 days
30-39	4	4
40-49	33	28
50-59	53	49
60-69	9	11
70-79	0	3
80-upward	0	0

### Calculation of Unitage

If desired, the results may be calculated to unitage values. For the purpose of statistical appraisal of the method, an empirical unit has been designated as that amount of vitamin B<sub>1</sub> which will effect a cure of the paralytic symptoms in 75 per cent or more but not less than 4 rats within a period of 48 hours, and wherein a period of at least 4 days, following the complete cure from the previous dose, elapses before recurrence of the paralytic reactions. In running an assay, different levels of the unknown should be fed, one level of which will produce cure as defined in 75 per cent or more but not less than 4 rats. The reference standard should also be fed concurrently at such a level as will produce cures in 75 per cent or more but not less than 4 rats. Unitage in terms of the reference standard may be calculated by the usual formula.

### Results and Comments

The above method applied in a critical and comparative study of vitamin B<sub>1</sub> reference standards yielded results which are presented and discussed below. The typical group of animals which is the subject of the following comments comprised 100 individuals equally divided as to sex. These individuals involved two subordinate groups of 56 and 44 obtained from different mating and litter periods. Death prior to the first paralytic reaction occurred with only 5 per cent and one of these was from accidental cause. Acceptable polyneuritic reactions previously described as of medium severity were manifested one or more times in 89 per cent of

TABLE II. WEIGHT GAIN DURING FOUR DAYS FOLLOWING DOSAGE WITH VITAMIN B<sub>1</sub>

Number of Observations	International Units	Weight Gain Grams
8	0.6	1.6
96	0.8	2.0
146	1.0	2.6
101	1.2	3.1
9	1.6	4.5

TABLE III. CURE OF PARALYTIC REACTIONS BY STANDARD VITAMIN B<sub>1</sub> PREPARATIONS

Test Substance	Amount of Dose	Number of Doses	Cured
	$\gamma$		%
Vitamin B <sub>1</sub> crystals	2.0	6	33
	2.6	34	65
	3.0	57	75
	3.4	3	67
	4.0	9	100
<i>Mg.</i>			
U. S. P. standard clay	6	7	0
	8	61	57
	10	78	60
	12	28	75
International standard clay	14	1	100
	6	13	62
	8	47	60
	10	58	67
	12	18	89

the animals within a period of 70 days, with an average period of 48 days as the time of the first reaction. The number of reactions per animal during a 115-day observation period was 4.9; the total number of acceptable reactions for the 89 reacting animals was 435. The maximum number of reactions per animal was 10.

Substantially constant weight was maintained throughout the 115-day observation period (Table I); 86 per cent of the animals did not exceed a weight of 59 grams after 42 days on the basal diet, and only 3 per cent had reached a weight of 79 grams after 70 days; 95 per cent of the animals weighed between 40 and 70 grams after 6 weeks and 88 per cent were within this weight range after 10 weeks. The vitamin B<sub>1</sub> dosage stimulated a weight gain during a period of about 4 days, commensurate with the amount of vitamin B<sub>1</sub> fed. Following the peak gain, gradual decline in weight resulted. If weight curves were plotted for those animals which exhibited a succession of reactions followed by doses of vitamin B<sub>1</sub>, such curves would show a characteristic saw-tooth form. Table II shows the correlation between weight gain during the 4-day period following dosage and the amount of vitamin B<sub>1</sub> expressed as International Units.

Table III contains the summarized data showing the degree of cure of the polyneuritic reaction resulting from variable amounts of pure vitamin B<sub>1</sub> crystals, U. S. P. standard clay, and International standard clay. From these data it is concluded that the two standard clays are of equal potency in vitamin B<sub>1</sub> content, each requiring 12 mg. to effect a cure in 75 per cent or more of the animals; and that 3 $\gamma$  of crystalline vitamin B<sub>1</sub> have the same curative effect for the specific symptoms as the 12-mg. quantities of the standard clays. These results, transposed to the gravimetric amount of each of the test substances required for the empirical unit as defined above, mean that 83 of such units are contained in 1 gram of each of the standard clays and 333,333 units are contained in 1 gram of pure vitamin B<sub>1</sub>.

A review of the data obtained with the standardized method for vitamin B<sub>1</sub> determinations as presented herein shows highly satisfactory results from the standpoint of high percentage yield of acceptable reacting animals, a relatively high number of acceptable reactions per animal, manifestation of clear-cut polyneuritic symptoms, and maintenance of a uni-



formly satisfactory physical condition in spite of maintenance of constant or substantially constant weight throughout the observation period.

### Summary

On the basis of the data submitted, especially when appraised in comparison with the performance and response of groups of animals submitted to similar tests but with less control and standardization of the dietary components and supplements, it appears that the vitamin B<sub>1</sub> determination involving the specificity of the polyneuritic reactions may be standardized by employing a comparatively simple basal

diet supplemented with pure entities or proved concentrates as the source of other dietary essentials.

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## A Glass-Enclosed Magnetic Stirrer

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**S**TIRRING within an enclosed glass system is frequently desired and usually accomplished by means of a magnetic device. The diagram shows a design which has proved very satisfactory. The stirrer contains a sealed-in iron core and is

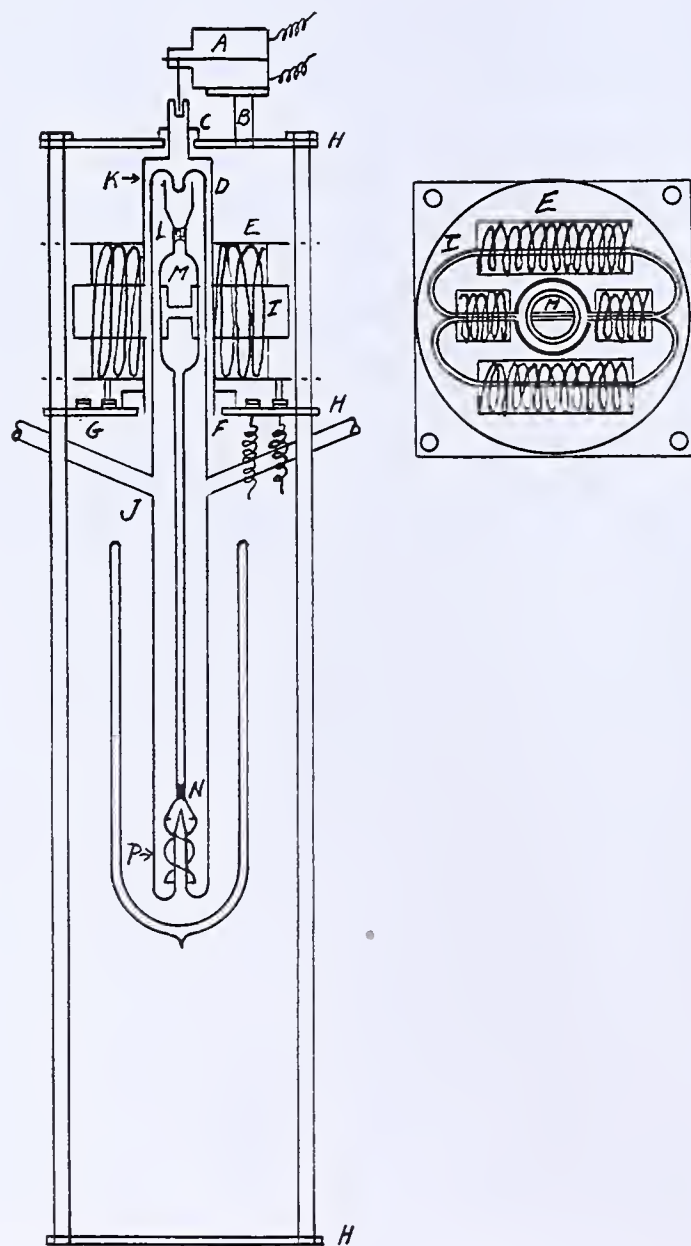
supported on glass bearings. The rotor which motivates it consists of a brass tube running in ball bearings and carrying a system of electromagnets. This is rotated by a small electric motor.

The glass tube, *J*, carrying side tubes for the admission of materials, has a small reëntering tube, *D*, at the top for a bearing and at the bottom has a larger reëntering tube terminating in a small fire-polished button that forms the lower bearing and supports the weight of the stirrer. The seals holding these bearing tubes must be smooth and well rounded. The stirrer has an open tube at the top into which the top bearing enters. Below that a larger tube contains the iron core, *M*, 0.6 cm. (0.25 inch) thick, which is H-shaped and is made of soft iron lamina riveted together. The shaft, made of 6-mm. tubing, is connected to the bottom of this larger tube, and terminates at the lower end in an inverted cone, *N*. The rim of this cone is thickened and to it are attached two rods, which are twisted and sealed to a ring of glass at the bottom to form the agitator, *P*. Tube *J* is made in two parts. The stirrer shaft is encased in copper screen or gauze and placed in *J*. The final seal can then be made without bending the shaft, and the copper is removed with nitric acid.

The magnets, *E*, are made of rectangular brass bobbins wound with No. 18 B. & S. insulated copper wire. The core, *I*, is of soft iron lamina which is 0.6 cm. (0.25 inch) thick through the central magnets and 0.3 cm. (0.125 inch) thick through the outer ones. This core enters slots in the wall of the brass tube, *K*. Brass disks above and below the magnets are securely fastened to the bobbins. The frame is made of four 1.25-cm. (0.5-inch) brass rods about 75 cm. (2.5 feet) long, held with three pieces of 0.3-cm. (0.125-inch) boiler plate, *H*, 17.5 × 17.5 cm. (7 × 7 inches). The bottom and middle plates are securely fastened, but the top plate is held with nuts to enable the magnet assembly to be removed. The brass tube, *K*, 5 cm. (2 inches) in diameter, rests on a thrust ball bearing, *F*, and has a 1.25-cm. (0.5-inch) brass shaft at the top, which is guided by the ball bearing, *C*. Insulated rings of brass, *G*, make electrical contact with carbon brushes connected to the magnets. The rotating assembly is carefully balanced to eliminate vibration. The motor support, *B*, contains clamps with which to secure the motor, *A*. This is a small inexpensive constant-speed motor with reducing gears. Motors of a great variety of speeds can be obtained, and changing the speed of stirring is accomplished by changing the motor.

A magnetic stirrer of this design has been very useful in studying the chemical reactions of small quantities of valuable gases. The inverted form of the lower bearing, *N*, prevents solid materials from interfering with the rotation. The reëntering tube with rounded seal resists thermal shock, and the tube withstands being plunged into liquid air. Mechanical strength is good, and the device has been used with internal pressures up to five atmospheres.

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# Nitric Acid Parting of Silver Assay Beads

## Containing the Platinum Metals and Gold

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THIS investigation was made to provide facts concerning the influence of the platinum metals and gold on certain phases of the nitric acid parting of the silver-precious metals beads. The authors have consistently stressed the fact that the assay bead is usually a polycomponent system and very few data are available from which one can even roughly predict the amount of precious metal dissolved by the acid.

Davis (1) reports a method for the separation of the precious metals in silver assay beads by the use of nitric acid, but gives no information regarding the effect of the presence of gold and the other platinum metals on the proportions of platinum and palladium dissolved by the parting acid. In investigating this phase of the parting, the authors have used the nitric acid concentrations and the silver ratio recommended by Davis.

### Preparation and Analysis of the Beads

The samples of spectrographically pure precious metal sponges and silver foil were wrapped in 25 grams of lead assay foil, compressed in a mold under a pressure of about 100 kg. per sq. cm., and cupeled at a cupel temperature of  $900^{\circ} \pm 25^{\circ} \text{C}$ . To assist in the removal of lead, the beads were left in the muffle for 2 minutes after "the blink." Owing to losses, the ratio of silver to the precious metals was usually between 14 to 1 and 15 to 1 after cupellation.

TABLE I. PLATINUM AND PALLADIUM IN FIRST NITRIC ACID SOLUTION

Sample	Silver Added Mg.	Platinum Added Mg.	Other Precious Metal Added Mg.	Silver Recovered Mg.	Loss of Silver Mg.	Precious Metals in Parting Acid Mg.
1	675.0	15.0	30.0 Au	633.9	41.1	13.9 Pt
2	255.0	15.0	2.0 Ru	242.7	12.3	6.3 Pt
3	255.0	15.0	2.0 Rh	245.4	9.6	7.9 Pt
4	255.0	15.0	2.0 Ir	246.8	8.2	8.6 Pt
5	255.0	15.0	2.0 Pd	240.6	14.4	9.5 Pt, 1.5 Pd
6	255.0	15.0	...	241.8	13.2	7.0 Pt
7	450.0	15.0	15.0 Pd	436.9	13.1	10.7 Pt, 13.9 Pd
8	675.0	15.0	30.0 Pd	656.0	19.0	7.1 Pt, 28.6 Pd
9	450.0	15.0	15.0 Au	437.2	12.8	12.2 Pt
10	255.0	15.0	2.0 Au	241.5	13.5	9.4 Pt
11	225.0	15.0	...	213.0	12.0	6.8 Pt
12	675.0	15.0	30.0 Au	651.2	23.8	12.2 Pt
13	450.0	15.0	15.0 Ir	425.5	24.5	5.6 Pt
14	450.0	15.0	15.0 Rh	433.6	16.4	3.8 Pt
15	450.0	15.0	15.0 Ru	430.0	20.0	5.1 Pt
16	275.0	15.0	15.0 Au	263.1	11.9	12.8 Pt

The beads were cleaned with dilute acetic acid and parted, first with 25 cc. of nitric acid (1 to 4), then with 25 cc. of nitric acid (1 to 1), and finally with 25 cc. of nitric acid (2 to 1). The three combined parting acids were evaporated on a steam bath to a volume of about 10 cc. to remove most of the nitric acid, diluted with water to 100 cc., and filtered, and the silver was precipitated with a few drops of hydrochloric acid.

After standing overnight the coagulated silver chloride was filtered through a Whatman's No. 42, 7-cm. filter paper. The precipitate and filter paper were heated with 20 cc. of concentrated sulfuric acid to which three 10-cc. portions of concentrated nitric acid were added. This treatment destroyed organic matter and dissolved the silver chloride. When the solution was dried almost to dryness, the residual silver sulfate was dissolved in 100 cc. of hot water, and the silver chloride was reprecipitated. The chloride was then filtered through a 15-cc. No. A<sub>2</sub> filtering crucible, dried at  $140^{\circ} \text{C}$ ., and weighed.

The filtrates from the two silver precipitations were combined and taken almost to dryness on the steam bath. The moist residue was evaporated three times with concentrated hydrochloric acid and then dissolved in 50 cc. of water. The acidity of this solution was adjusted to pH 4 by means of a filtered 10 per cent sodium bicarbonate solution using bromophenol blue as the indicator. Two cubic centimeters of a filtered 10 per cent sodium bromate solution were added and, after boiling for 15 minutes to oxidize the platinum, the solution was adjusted to an acidity of pH 6, using bromocresol purple as indicator. Any

precipitate, which would consist of the dioxides of palladium, rhodium, etc., as well as compounds of base metals such as lead and iron, was filtered out and then dissolved in 4 cc. of hot hydrochloric acid (1 to 1). To remove traces of platinum this solution was diluted, adjusted in acidity to pH 4, boiled with sodium bromate, and adjusted to pH 6. The precipitate was filtered out and, if necessary, subsequently treated for palladium.

The filtrates from the two dioxide precipitations were combined and taken almost to dryness on the steam bath, excess bromate being destroyed by additions of concentrated hydrochloric acid. The residue was dissolved in about 150 cc. of water and the acidity adjusted to about pH 8. Boiling at this pH caused more complete precipitation of any lead and iron present which would contaminate the platinum. The solution was then filtered, adjusted to pH 6, and boiled for an hour with sodium formate to precipitate the platinum. The metal was filtered through a Whatman's No. 42, 7-cm. filter paper, washed with 0.01 N hydrochloric acid to dissolve base metal precipitates, and finally with 1 per cent ammonium chloride solution. After burning in a 5-cc. porcelain crucible, the residue was cooled and weighed as platinum.

Palladium, when present in the parting acid, was precipitated at pH 6. After reprecipitation to remove platinum contamination, the dioxide was dissolved in 4 cc. of hot hydrochloric acid (1 to 1), and diluted to about 100 cc. with water, and palladium was precipitated with dimethylglyoxime. The precipitate was filtered through a Whatman's No. 42, 11-cm. filter paper, washed, and burned wet in a 15-cc. porcelain crucible. The residue, after reduction in hydrogen and cooling in carbon dioxide, was weighed as palladium.

The results obtained on parting a series of silver assay beads according to the above directions are reported in Table I. The residues were inquartated, cupeled, and parted until the amount of platinum and palladium extracted by the parting acid was very small. Results for the second and third partings are recorded in Tables II and III.

TABLE II. PLATINUM AND PALLADIUM IN SECOND NITRIC ACID SOLUTION

Sample	Precious Metals Left after First Parting Mg.	Silver Added Mg.	Silver Recovered Mg.	Loss of Silver Mg.	Precious Metals in Parting Acid Mg.
1	31.1	455.0	451.5	3.5	1.0 Pt
2	10.7	170.0	164.4	5.6	5.4 Pt
3	9.1	140.0	129.1	10.9	4.3 Pt
4	8.4	140.0	132.6	7.4	4.0 Pt
5	6.0	95.0	88.4	6.6	3.2 Pt, 0.5 Pd
6	8.0	120.0	107.7	12.3	4.5 Pt
7	5.4	95.0	91.8	3.2	3.6 Pt, 1.0 Pd
8	9.3	155.0	137.5	17.5	4.7 Pt, 1.2 Pd
9	17.8	270.0	258.0	12.0	2.6 Pt
10	7.6	130.0	123.8	6.2	3.7 Pt
11	8.2	125.0	118.7	6.3	5.6 Pt
12	32.8	495.0	483.9	11.1	2.8 Pt
16	17.2	85.0	82.2	2.8	2.1 Pt

TABLE III. PLATINUM AND PALLADIUM IN THIRD NITRIC ACID SOLUTION

Sample	Precious Metals Left after Second Parting Mg.	Silver Added Mg.	Silver Recovered Mg.	Loss of Silver Mg.	Precious Metals in Parting Acid Mg.	Total Pt and Pd Recovered after 3 Partings Mg.
2	5.3	85.0	82.8	2.2	3.4 Pt	15.1 Pt
3	4.8	72.0	65.7	6.3	0.1 Pt	12.3 Pt
4	4.4	66.0	65.0	1.0	Nil	12.6 Pt
5	2.3	71.0	70.0	1.0	{ 2.2 Pt 0.0 Pd	{ 14.9 Pt 2.0 Pd
6	3.5	55.0	50.8	4.2	3.4 Pt	14.9 Pt
7	0.8	12.0	9.6	2.4	{ 0.7 Pt 0.0 Pd	{ 15.0 Pt 14.9 Pd
8	3.4	80.0	76.6	3.4	{ 1.8 Pt 0.0 Pd	{ 13.6 Pt 29.8 Pd
10	3.9	25.0	24.2	0.8	1.0 Pt	14.1 Pt
11	2.6	40.0	38.2	1.8	2.0 Pt	14.4 Pt



Any final residues after the last parting were treated with aqua regia, and the platinum and palladium, if any, were determined as above.

### Extraction of Platinum from Binary and Ternary Systems

**SILVER-PLATINUM.** The results reported in the tables for samples 6 and 11, each containing 15.0 mg. of platinum, indicate that at least three successive partings with nitric acid are necessary to dissolve most of the platinum. The weights of platinum recovered from the aqua regia solutions of the residues from the third partings were nil and 0.4 mg., respectively; hence, the total recovery for sample 6 was 14.9 mg. and for sample 11, 14.8 mg.

**SILVER-PLATINUM-PALLADIUM.** Sample 5, containing 15.0 mg. of platinum and 2.0 mg. of palladium, required two nitric acid partings to dissolve all the palladium. A total of 14.9 mg. of platinum was recovered after three partings and the aqua regia solution of the residue yielded no platinum. Bead 7, containing 15.0 mg. each of platinum and palladium, required two nitric acid partings to dissolve 14.9 mg. of the palladium and three partings to dissolve 15.0 mg. of platinum. Sample 8, containing 15.0 mg. of platinum and 30.0 mg. of palladium, yielded 29.8 mg. of palladium after two partings and 13.6 mg. of platinum after three partings. The residue of sample 8 was dissolved in aqua regia and yielded 1.5 mg. of platinum, a total platinum recovery of 15.1 mg.

TABLE IV. PALLADIUM IN FIRST NITRIC ACID SOLUTION

Sam- ple	Palladium Added Mg.	Other Precious Metal Added Mg.	Silver Added Mg.	Silver Recovered Mg.	Loss of Silver Mg.	Palladium Recovered Mg.
1	15.0	15.0 Rh	460.0	448.2	11.8	12.8
2	15.0	15.0 Ir	460.0	446.1	13.9	12.6
3	15.0	15.0 Ru	460.0	445.9	14.1	13.5
4	15.0	15.0 Au	280.0	270.4	9.6	15.0
5	15.0	30.0 Au	325.0	315.4	9.6	15.1
6	15.0	...	230.0	219.8	10.2	15.0

**SILVER-PLATINUM-GOLD.** The presence of gold in the assay bead seems to assist the dissolving of platinum rather than hinder it. This has been discussed by Smith (2). Bead 1, containing 30.0 mg. of gold and 15.0 mg. of platinum, required only two nitric acid partings to dissolve 14.9 mg. of platinum. Sample 9, containing 15.0 mg. each of platinum and gold, required two partings to dissolve 14.8 mg. of platinum. With sample 10, containing 15.0 mg. of platinum and 2.0 mg. of gold, three partings yielded 14.1 mg. of platinum and subsequent aqua regia treatment 1.0 mg. more. When the silver ratio was reduced as in the case of bead 16, containing 15.0 mg. each of platinum and gold, two partings dissolved 14.9 mg. of platinum.

**SILVER-PLATINUM-IRIDIUM.** The presence of iridium in the assay bead seems to lessen the dissolving of platinum in the parting acid.

Sample 4, containing 15.0 mg. of platinum and 2.0 mg. of iridium, yielded 12.6 mg. of platinum after three partings. The aqua regia solution of the final residue yielded 2.7 mg. more, making a total recovery of 15.3 mg. of platinum. Bead 13, containing 15.0 mg. each of platinum and iridium, produced 5.6 mg. of platinum from the first parting acid.

**SILVER-PLATINUM-RHODIUM.** Rhodium also seems to retain platinum in the parting of assay beads. Sample 3, containing 15.0 mg. of platinum and 2.0 mg. of rhodium, yielded a total of 12.3 mg. of platinum after three partings and a further 2.5 mg. by the aqua regia treatment, making a total recovery of 14.8 mg. From the first parting acid of bead 14, containing 15.0 mg. of both platinum and rhodium, 3.8 mg. of platinum were recovered.

**SILVER-PLATINUM-RUTHENIUM.** Ruthenium also seems to lessen the dissolving of platinum in the parting acid. Sample 2, containing 15.0 mg. of platinum and 2.0 mg. of ruthenium, yielded 15.1 mg. of platinum after three partings. Bead 15, which contained 15.0 mg. of both platinum and ruthenium, produced 5.1 mg. of platinum from the first parting acid.

### Extraction of Palladium from Binary and Ternary Systems

**SILVER-PALLADIUM.** The result for sample 6 (Table IV) indicates that one nitric acid parting is sufficient to dissolve completely the palladium in a bead containing the reported amounts of silver and palladium.

**SILVER-PALLADIUM-PLATINUM.** The effect of the presence of platinum in the assay bead on palladium extraction has been discussed in the preceding section.

**SILVER-PALLADIUM-GOLD.** The results for samples 4 and 5 (Table IV) indicate that gold does not prevent the dissolving of palladium in the parting acid. A single parting was sufficient in each case.

**SILVER-PALLADIUM-IRIDIUM.** Iridium causes retention of palladium in the residue from the first parting. Bead 2 (Table IV), containing 15.0 mg. each of palladium and iridium, required two partings to recover 14.9 mg. of palladium.

**SILVER-PALLADIUM-RHODIUM.** Rhodium, like iridium, lessens the dissolving of palladium in nitric acid. Bead 1 (Table IV), containing 15.0 mg. of both palladium and rhodium, yielded 12.8 mg. of palladium from the first parting acid. The second parting acid contained 259.0 mg. of silver and 2.1 mg. of palladium, making a total palladium recovery of 14.9 mg.

**SILVER-PALLADIUM-RUTHENIUM.** Ruthenium also causes the retention of palladium. The first parting acid of bead 3 (Table IV) produced 13.5 mg. of palladium. The second parting acid yielded 250.9 mg. of silver and 1.6 mg. of palladium; the total palladium recovery was 15.1 mg.

### Extraction of Platinum and Palladium from Polycomponent Systems

An assay bead was prepared from 15.0 mg. of gold, 15.0 mg. of platinum, 15.0 mg. of palladium, 1.0 mg. each of iridium, rhodium, and ruthenium, and 550.0 mg. of silver. The silver recovered after cupellation weighed 532.5 mg. The platinum recovered from the first parting acid weighed 8.6 mg. and the palladium 14.8 mg.

A second assay bead was prepared from 30.0 mg. of gold, 15.0 mg. of platinum, 5.0 mg. of palladium, 0.5 mg. each of iridium, rhodium, and ruthenium, and 430.0 mg. of silver. The first parting acid contained 424.4 mg. of silver, 7.6 mg. of platinum, and 5.0 mg. of palladium.

These beads roughly represent proportions of the platinum metals and gold often found in platinum ores.

### Observations

The color of the nitric acid extract is no indication of the proportion of platinum present. Solutions containing very appreciable amounts of platinum were water-white.

Under the conditions described a considerable amount of platinum is often precipitated at pH 6 despite sodium bromate treatment; a reprecipitation is therefore necessary.

Base metals such as iron, which may be introduced through the reagents, and residual lead from the assay bead precipitate at pH 6 and contaminate the platinum. Preliminary adjustment to about pH 8 favors the complete precipitation of the base metals. The solution, after filtering, is adjusted to pH 6 to separate the palladium.



### Summary

When a bead with a silver-platinum ratio of about 15 to 1 is parted with nitric acid, even three successive treatments will not always dissolve all the platinum.

Beads containing only silver and palladium with the above silver ratio require only one parting with nitric acid to dissolve the palladium completely.

The presence of gold in the assay bead seems to assist the dissolving of platinum and palladium in the nitric acid.

Iridium, rhodium, and ruthenium definitely interfered with the dissolving of platinum and palladium in the parting acid.

The presence of platinum in the bead decreased the action of the first parting acid on palladium.

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## A Rapid Method for Gold in Cyanide Plating Solutions

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IN DETERMINING the gold content of cyanide electroplating solutions for control or evaluation purposes, most of the commonly known methods are too long drawn out or involved to be of routine use to the practical analytical chemist who must make many such determinations each day. The evaporation method (5), the copper sulfate method (4), the zinc-lead acetate method (1), and the hydrochloric-ferrous sulfate method (2) were found by the author to be unsuitable because of the excessive amount of time or the tedious operational procedure required.

A method suggested by Weisberg (7) proved to be sufficiently speedy (an analysis can be made in 2 hours) and simple but lacked accuracy, as some of the gold precipitated in colloidal form and could not be retained on a filter paper or matting. However, further experimentation resulted in the improved method described in this paper.

### Determination of Gold

**WEISBERG PROCEDURE.** After thorough stirring, permitting any sediment to settle, pipet a 50-ml. sample into a 500-ml. Erlenmeyer flask. Place the flask under a good draft hood and cautiously add concentrated sulfuric acid until vigorous action ceases. Add 50 ml. more of acid and place the flask over heat, boiling for about 45 minutes until all the gold has precipitated in brown sponge form. Boil 5 to 10 minutes longer to coagulate the gold. Cool the flask and filter into a tared Gooch crucible, carefully washing all particles of gold onto the filter. Wash with hot dilute sulfuric and then with hot water until the washings are no longer acid. Dry and ignite in the Gooch until the brown sponge turns golden yellow in color. Cool to room temperature and weigh.

Invariably a small but definite amount of gold precipitated in such a finely divided state as to pass through the asbestos filter mat of the Gooch, even after continued matting with gold. This was evidenced by the faint bluish brown color of the filtrate and the presence of the Tyndall effect on examination of the filtrate in a beam of light.

That the gold came down in part in a colloidal state could only have been due to the weak ionization of the concentrated sulfuric acid. This was proved by the fact that, if the sulfuric acid containing the gold in finely divided form was diluted with a large volume of water and further boiled, most of this colloidal gold precipitated. However, this change in method was hardly feasible because of the danger of explosion and spattering, the additional time required, and the fact that the colloidal gold was not completely precipitated.

The author found that whenever silver was present in the electroplating solution (green gold), the gold almost always

came down perfectly and the supernatant sulfuric acid was crystal clear and showed no Tyndall effect. It was decided that this perfect precipitation was brought about by a mutual suspensoid precipitation—i. e., the type that occurs when a suspensoid solution of ferric hydroxide is mixed with a suspensoid solution of arsenic trisulfide—the assumption being that the particles of silver formed in the early part of the process neutralize the charges on the finely divided gold particles and precipitate with them in a coagulated mass from which the silver dissolves on further boiling with sulfuric acid, leaving the gold in sponge form. If so, then adding a measured amount of a soluble silver salt to a sample containing only gold, prior to the addition of the sulfuric acid, would bring about the same results. This was found to be the case.

Several experiments showed that a wide latitude in the amount of silver salt was possible without ill effects, but in general the optimum amount of silver nitrate solution that could be added was just sufficient to combine with the free cyanide present in the electrogilding solution. With this in view, the method of Weisberg was revised as follows:

**REVISED PROCEDURE.** If the solution to be tested is high in gold content (0.5 to 20 grams per liter) take a 10-ml. sample; if low in gold content (0.5 gram or less per liter), take a proportionally greater sample. Transfer sample to a 500-ml. Erlenmeyer flask, dilute with 50 ml. of pure water, and add sufficient 0.1 N silver nitrate from a buret to combine completely with the free cyanide, using 5 ml. of a 2 per cent solution of potassium iodide as indicator (this is the equivalent of Liebig's method for the determination of free cyanide, 6). Place the flask under a good draft hood and cautiously add concentrated sulfuric acid until vigorous action ceases. Now add 50 ml. more of sulfuric acid and heat the flask to boiling, adjusting the flame so that the ebullition does not become too violent. Discontinue heating the moment the precipitate of gold turns light brown in color and the sulfuric acid is absolutely clear.

Decant the supernatant acid and treat the precipitate with 50 ml. more of concentrated sulfuric acid, heating to the boiling point to dissolve any silver sulfate that may be present. Decant this acid, leaving as little as possible in the flask. Carefully dilute the remaining acid with 200 ml. of distilled water and filter the contents onto a tared Gooch crucible lined with asbestos. Wash the precipitate with hot dilute sulfuric and then with hot water until the washings are no longer acid. Dry and ignite at red heat until the brown sponge turns golden yellow. Cool to room temperature and weigh.

To compare the accuracy of this method with that of the evaporation method, tests were made on standard samples prepared as follows:

c. p. gold weighed accurately to within 0.1 mg. was dissolved in a minimum amount of aqua regia and carefully evaporated



to small volume three times to drive off the excess nitric acid. This was diluted with water to about 250 ml. and sufficient c. p. potassium cyanide was dissolved in it to supply the free cyanide content of the average gold plating bath (about 10 grams per liter, 3) upon dilution to 1 liter. This solution was now carefully transferred to a 1-liter volumetric flask and carefully diluted to the mark with distilled water.

TABLE I. ACCURACY OF METHODS

Sample	Weight G./l.	Evaporation Method	Difference Mg.	Sulfuric Method G./l.	Difference Mg.
		G./l.			
1	0.1050	0.1048	-0.2	0.1051	+0.1
2	0.5001	0.4999	-0.2	0.4998	-0.3
3	5.0045	5.0044	-0.1	5.0044	-0.1
4	20.0100	20.0099	-0.1	20.0098	-0.2
		Av. -0.15		Av. -0.13	

Four samples prepared this way were analyzed by both methods with the results given in Table I. This comparison shows that the sulfuric acid method is accurate for routine determinations of gold in cyanide plating solutions. In actual laboratory practice the author has used this method with great success during the past year, his evaluation analyses closely checking with those of the chemists of submitting firms.

The method will be found very convenient in control analyses, as from one sample the following determinations may be made: free cyanide, gold, silver if any (by precipitating silver in filtrate with hydrochloric acid and subtracting the known amount of silver added), and other base metals such as copper, nickel, and zinc, by analyzing the filtrate according to standard methods.

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## *p*-Hydroxyphenylarsonic Acid as a Reagent for Titanium and Zirconium

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SEVERAL investigators have reported the value of certain arsonic acids as reagents for the gravimetric determination of zirconium (2, 4, 5), thorium (4), tin (3), and iron (1). The need for a reagent that would give a convenient and satisfactory separation of titanium from the common elements, and particularly from iron, led to a further investigation of this field.

*p*-Hydroxyphenylarsonic acid was found to be a very favorable reagent for titanium. In the presence of dilute mineral acid it gives an effective separation of titanium from iron and most other commonly occurring elements in one precipitation. It is also an excellent reagent for zirconium. In mineral acid solutions not stronger than 0.5 *N* it also gives a quantitative precipitation of tin, but the possibility of using it as a reagent for this element has not been investigated in detail.

### Determination of Titanium

**MATERIALS.** The *p*-hydroxyphenylarsonic acid used in this investigation was supplied by the Mallinckrodt Chemical Works and was suitable for use without further purification. A 4 per cent aqueous solution was found to be convenient for use. Pure standard solutions of titanium sulfate were prepared and standardized by accepted methods. All other reagents were of c. p. or equivalent grade.

**PROCEDURE.** Dissolve the sample (containing not more than about 0.06 gram of titanium dioxide) in hydrochloric or sulfuric acid solution and remove interfering elements by appropriate means. The amount of acid present should be such that the solution will be approximately but not more than 0.60 *N* in hydrochloric or 1.80 *N* in sulfuric acid after the reagents have been added and the precipitation is complete. After adjusting the volume to about 200 cc., heat the solution to boiling and (after the addition of 2 to 3 grams of ammonium thiocyanate when iron is present) add 100 cc. of a 4 per cent aqueous solution of *p*-hydroxyphenylarsonic acid. Continue boiling gently for at least 15 minutes to coagulate the precipitate and thus facili-

tate filtering. After cooling to room temperature filter off the precipitate. With a good paper (No. 42 Whatman) and a filter cone one may employ suction advantageously.

Wash the precipitate about five or six times with a wash liquor of dilute (0.25 *N*) hydrochloric or sulfuric acid containing about 0.5 gram of reagent per 100 cc. When iron is present 1 or 2 grams of ammonium thiocyanate should also be added to each 100 cc. of this liquor. Finally wash the precipitate two or three times with a dilute (2 per cent) aqueous solution of ammonium nitrate, and then ignite it in a porcelain crucible (with propped lid) at low temperature until all the carbon is burned off, then at the full heat of a Bunsen or Fisher burner until constant weight is attained, leaving a residue of titanium dioxide. The ignition must be carried out in an efficient fume hood.

An average deviation of 0.7 part per thousand was found in analyzing pure standard solutions of titanium by this method.

### Separation of Titanium from Mixtures

**IRON AND PHOSPHATE.** A synthetic sample (containing 0.0636 gram of TiO<sub>2</sub>, 0.4392 gram of Fe<sub>2</sub>O<sub>3</sub>, and 0.071 gram of P<sub>2</sub>O<sub>5</sub>) was analyzed by the above procedure for titanium, with a recovery of 0.0636 gram of titanium dioxide. Another sample, containing the same amount of titanium and iron but no phosphate, gave the same result.

**ALUMINUM, ZINC, COBALT, NICKEL, BERYLLIUM, AND BASIC CHROMIUM AND MANGANESE.** From a composite sample (containing 0.0521 gram TiO<sub>2</sub>, 0.051 gram of Al<sub>2</sub>O<sub>3</sub>, 0.063 gram of Cr<sub>2</sub>O<sub>3</sub>, 0.079 gram of MnO, 0.081 gram of ZnO, 0.075 gram of CoO, 0.075 gram of NiO, and 0.030 gram of BeO) 0.0521 gram of titanium dioxide was easily separated. From another such mixture containing 0.0636 gram of titanium dioxide this procedure returned 0.0636 gram.

**CALCIUM AND MAGNESIUM.** Two samples containing, respectively, 0.0521 and 0.0636 gram of titanium dioxide with a mixture of 0.056 gram of calcium oxide and 0.040 gram of magnesium oxide were analyzed. The results were 0.0521 and 0.0636 gram of titanium dioxide.

**DICHROMATE, PERMANGANATE, URANYL, AND VANADYL IONS.** A composite sample (containing 0.0636 gram of TiO<sub>2</sub>, 0.052 gram of Cr<sub>2</sub>O<sub>3</sub>, 0.071 gram of MnO, 0.180 gram of V<sub>2</sub>O<sub>5</sub>, and 0.286

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gram of  $\text{UO}_3$ ) was used. It was necessary to use 5 rather than the usual 4 grams of reagent to secure a quantitative precipitation. Otherwise the separation was normal, 0.0636 and 0.0637 gram being found in duplicate analyses.

**MOLYBDATE.** No difficulty was experienced in separating 0.0636 gram of titanium dioxide from 0.071 gram of molybdenum oxide present as ammonium molybdate. Duplicate analyses gave 0.0637 and 0.0639 gram of titanium dioxide.

**THALLIUM AND CERIUM (CEROUS).** The separation of 0.0636 and 0.0521 gram of titanium dioxide, respectively, from 0.213 gram of cerous oxide (present as cerous nitrate) mixed with 0.076 gram of thallic oxide was satisfactory, yielding 0.0637 and 0.0521 gram of titanium dioxide. However, cerium in the ceric form cannot be separated from titanium by this method.

**THORIUM.** Some difficulty was encountered here. Apparently thorium ties up some of the arsonic acid as an undissociated soluble complex, so that the regular procedure gives low results for titanium. It was found best to use sulfuric rather than hydrochloric acid, and also to use considerable excess of reagent. Using 6 grams of parahydroxyphenylarsonic acid and sulfuric acid solution, 0.0636 gram of titanium dioxide was easily separated from 0.0516 gram of thorium oxide by one precipitation, duplicate samples giving 0.0637 and 0.0638 gram of titanium dioxide.

**CHROME-VANADIUM STEEL.** A 2-gram sample of Bureau of Standards chrome-vanadium steel No. 30-C (containing 0.76 per cent  $\text{SiO}_2$ , 1.43 per cent  $\text{Cr}_2\text{O}_3$ , 0.64 per cent  $\text{MnO}$ , 0.10 per cent  $\text{NiO}$ , 0.045 per cent  $\text{P}_2\text{O}_5$ , 0.19 per cent  $\text{MoO}_3$ , and 0.125 per cent  $\text{CuO}$ ) was dissolved in dilute hydrochloric acid and the silica was removed in the usual way. Then, since the sample contained no titanium, 25 cc. of a solution of titanium sulfate containing 0.0521 gram of titanium dioxide were added, followed by 5 grams of ammonium thiocyanate. The titanium was then precipitated and determined as usual. The ignited residue was white, containing no trace of iron oxide. Duplicate samples each gave a recovery of 0.0521 gram of titanium dioxide.

**IRON ORE.** Four separate 5-gram samples of Bureau of Standards iron ore No. 29 (containing 12.02 per cent  $\text{SiO}_2$ , 1.91 per cent  $\text{Al}_2\text{O}_3$ , 0.08 per cent  $\text{V}_2\text{O}_5$ , 0.09 per cent  $\text{MnO}$ , 2.90 per cent  $\text{CaO}$ , 2.01 per cent  $\text{MgO}$ , 0.51 per cent  $\text{K}_2\text{O}$ , 0.45 per cent  $\text{Na}_2\text{O}$ , and 0.99 per cent  $\text{TiO}_2$ ) were taken up with 100 cc. of dilute hydrochloric acid and filtered, and the undissolved residue was fused with sodium carbonate. The fusion was washed into the main filtrate and after removing the silica in the usual manner, 5 grams of ammonium thiocyanate were added, the solution was diluted to 300 cc., and the titanium was precipitated with 4 grams of *p*-hydroxyphenylarsonic acid dissolved in 100 cc. of water. The analysis was finished in the usual way. The titanium dioxide results were 0.964, 0.970, 0.970, and 0.976 per cent, respectively.

**BURNT REFRACTORY.** Bureau of Standards burnt refractory No. 78 (20.69 per cent  $\text{SiO}_2$ , 59.97 per cent  $\text{Al}_2\text{O}_3$ , 0.79 per cent  $\text{Fe}_2\text{O}_3$ , 0.51 per cent  $\text{MgO}$ , 0.38 per cent  $\text{CaO}$ , 2.83 per cent  $\text{K}_2\text{O}$ , 0.53 per cent  $\text{Na}_2\text{O}$ , 0.62 per cent  $\text{P}_2\text{O}_5$ , 0.047 per cent  $\text{V}_2\text{O}_5$ , 0.12 per cent  $\text{ZrO}_2$ , and 3.37 per cent  $\text{TiO}_2$ ) was used. Four 2-gram samples were run for titanium by the following procedure: The sample was fused with 15 grams of potassium pyrosulfate and the fusion was taken up with 100 cc. of water containing 9 cc. of concentrated sulfuric acid. The residue was filtered off, and the silica was volatilized with a mixture of hydrofluoric and sulfuric acids. The small remaining residue was again fused with a small amount of potassium pyrosulfate and then dissolved in the original filtrate. After filtration, the solution was diluted to 225 cc., 2 grams of ammonium thiocyanate were added, and the analysis for titanium was finished as usual with *p*-hydroxyphenylarsonic acid. The final titanium oxide figures were obtained by subtracting the Bureau of Standards figure for zirconium oxide from the weight of the mixed titanium and zirconium oxides found in the present work. The four results were 3.33, 3.34, 3.35, and 3.35 per cent of titanium dioxide, respectively. Bureau of Standards figures varied from 3.18 to 3.68 per cent of titanium dioxide, with an average of 3.37 per cent.

**PLASTIC CLAY.** Bureau of Standards plastic clay No. 98 [59.11 per cent  $\text{SiO}_2$ , 25.54 per cent  $\text{Al}_2\text{O}_3$ , 2.05 per cent  $\text{Fe}_2\text{O}_3$ , 0.08 per cent  $\text{P}_2\text{O}_5$ , 0.025 per cent  $\text{V}_2\text{O}_5$ , 0.021 per cent  $\text{Cr}_2\text{O}_3$ , 0.21 per cent  $\text{CaO}$ , 0.72 per cent  $\text{MgO}$ , 3.17 per cent  $\text{K}_2\text{O}$ , 0.28 per cent  $\text{Na}_2\text{O}$ , 0.07 per cent  $\text{SO}_3$ , 0.005 per cent  $\text{MnO}$ , 0.009 per cent  $\text{CuO}$ , 0.041 per cent  $\text{ZrO}_2$ , and 1.43 per cent  $\text{TiO}_2$  (average of several analyses varying from 1.35 to 1.50 per cent)] was analyzed for titanium. Triplicate 2-gram samples were fused with sodium carbonate, and taken up in dilute hydrochloric acid, and evaporated to dryness on a steam bath. The residue was extracted with dilute hydrochloric acid and the insoluble material was then filtered off and evaporated with a mixture of sulfuric and hydrofluoric acids to dryness, finally being fused again with a small amount of sodium carbonate. The fusion was dissolved in the original filtrate and ammonia was added until the solution re-

mained just slightly acid. Two grams of ammonium thiocyanate were added and the titanium was determined with *p*-hydroxyphenylarsonic acid in the usual way. After subtracting 0.041 per cent of zirconium oxide 1.41, 1.41, and 1.41 per cent of titanium dioxide was found.

**ZIRCONIUM.** The method already outlined for titanium precipitates zirconium as well, so that when both metals are present in the sample separate analyses must be made for each. The zirconium alone may be precipitated in the presence of excess hydrogen peroxide, while in a second sample the zirconium and titanium are both precipitated (in the absence of hydrogen peroxide) and determined as the mixed oxides. This is preferable to trying to determine the titanium in the filtrate containing hydrogen peroxide.

If it is desirable to run both zirconium and titanium on the same sample, the best procedure for determining the titanium in the filtrate from the zirconium is to evaporate to fumes, add nitric acid, and evaporate again to fumes. After taking up in water, the acidity is adjusted to the desired concentration with ammonia and the titanium is precipitated and determined by the procedure given above for titanium. Attempts to eliminate hydrogen peroxide without evaporating down to white fumes proved impractical.

The separation of zirconium from titanium is best effected in 2.5 to 3.0 *N* sulfuric acid solution. A large excess of hydrogen peroxide (15 to 20 cc. of 30 per cent solution) must be present to prevent titanium from being precipitated, and hydrogen peroxide should also be added to the wash liquor. Moreover, several times the usual quantity of reagent must be used. In separating 0.10 gram of zirconium oxide from 0.05 gram of titanium dioxide it was found necessary to employ 3.0 grams of reagent, instead of the usual 1.0 gram required to give a quantitative separation of this amount of zirconium from most of the common elements other than titanium.

The general procedure for determining zirconium is essentially the same as that outlined for titanium, except that a mineral acid concentration of 2.5 to 3.0 *N* is employed and less reagent is necessary. This method is particularly applicable to the determination of zirconium in the presence of a large amount of iron. Quantities of zirconium oxide ranging from 0.004 to 0.10 gram were quantitatively separated from 10 grams of the aforementioned chrome-vanadium steel in one precipitation. If present in more than very small amounts, phosphate interferes with the determination of zirconium by this method.

## Summary

*p*-Hydroxyphenylarsonic acid has been found an advantageous reagent for separating titanium from the following ions: ferric, ferrous, aluminum, zinc, cobalt, nickel, beryllium, chromic, manganous, calcium, magnesium, thallium, cerous, thorium, sodium, potassium, ammonium, as well as phosphate, molybdate, chromate, vanadate, permanganate, uranyl, and vanadyl. Interfering ions are zirconium, cerium (ic), and tin. Hydrogen peroxide also must be absent.

The reagent may be used to determine zirconium in the presence of the above ions. Phosphate in more than very small amounts interferes. Zirconium may be separated from titanium if hydrogen peroxide is present. Cerium (ic) and tin interfere.

## Acknowledgment

The authors are grateful to F. C. Whitmore, D. M. Jones, and the Mallinckrodt Chemical Works for making available certain valuable reagents used in this investigation.

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RECEIVED March 3, 1938.



# Glass-Blowing Accessories

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LABORATORY glass blowing offers so many difficulties that kinks and accessories developed by one amateur may be of interest to others. Several of these have proved of value in this laboratory, and are described below.

## Glass Blower's Mouthpiece

When working with glass it is often convenient to blow through a rubber tube attached to the apparatus, biting on the tube gently to hold it in place in the mouth. If the tubing is inadvertently clamped shut, closing off the entire system, the pressure may increase as the glass is heated until a bubble suddenly blows out, particularly if there is a thin spot in the glass.

The stem of an inexpensive pipe serves well as a mouthpiece, but sometimes the tongue comes to rest over the end of it, closing off the system with the same result as above.

Gases released from the glass itself and from decomposition of material present in the system may be projected into the mouth and inhaled. Ordinarily the gases are not objectionable. Harris and Schumacher (2) have reported that the main gases released by glass on heating are carbon dioxide and water, accompanied by smaller quantities of sulfur dioxide, oxygen, and nitrogen. However, if it becomes necessary to make repairs on an apparatus that cannot be cleaned thoroughly, many combinations of gases may be released by thermal decomposition of organic accumulations.

The mouthpiece shown in Figure 1 is designed to by-pass the gases by the same movement of the tongue that would ordinarily close off the system. The exact dimensions are not important, but a convenient size is indicated. The barrel, *A*, and the hose nipple, *B*, are turned from hard rubber, and either threaded or cemented together. The large bore in the barrel is made 0.47 cm. (0.187 inch) in diameter, and tapped with the U. S. Standard  $\frac{1}{4}$ -20 threads far enough to accommodate the brass sleeve, *C*. The outer end of the sleeve is cut to a cone to form a seat with the brass cap, *D*. A similar cap and seat, *E*, are made at the bit end of the barrel. The valves are seated by grinding with fine silicon carbide. The caps are soldered to a shaft, *F*, which consists of a suitable length of 0.12-cm. (0.047-inch) wire. A soft compression spring placed as shown and soldered to the shaft at *G* normally keeps valve *E* open. The bit is filed to a convenient shape, as shown at *H* in the end-view drawing at the left. Section *J* is deliberately made long, so that the valve extends into the mouth within easy reach of the tongue.

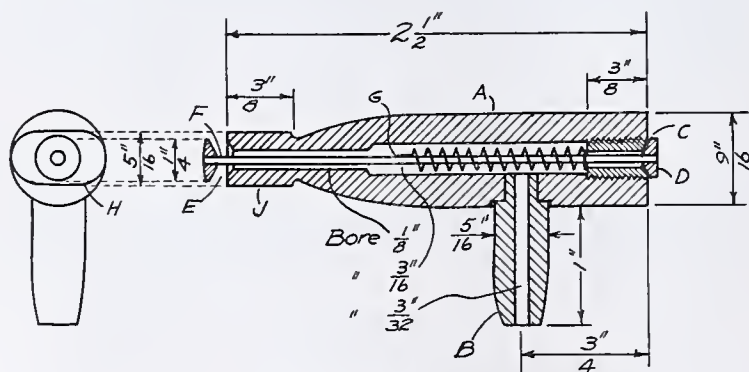


FIGURE 1. GLASS BLOWER'S MOUTHPIECE

In use the tongue closes valve *E* and simultaneously opens valve *D*, by-passing all the gases to the atmosphere. When blowing is to be done the tongue is removed, thus permitting the valves to reverse and connect the system with the mouth.

The mouthpiece may be clamped in proper position and lips applied when desired, as is the practice in some glass apparatus factories.

The author has used such a mouthpiece for 2 years and considers it a great convenience.

## Making Ground-Glass Joints

The amateur usually experiences considerable difficulty in making ground-glass joints. In the conventional procedure the outer cone is easily formed, using a polygonal carbon shaper (Figure 2, *a*), but the inner cone is prepared by alternate heating and pulling, the final form depending upon skill and guesswork. A poor fit between the cones requires a long grinding time and results in a joint with low mechanical strength.

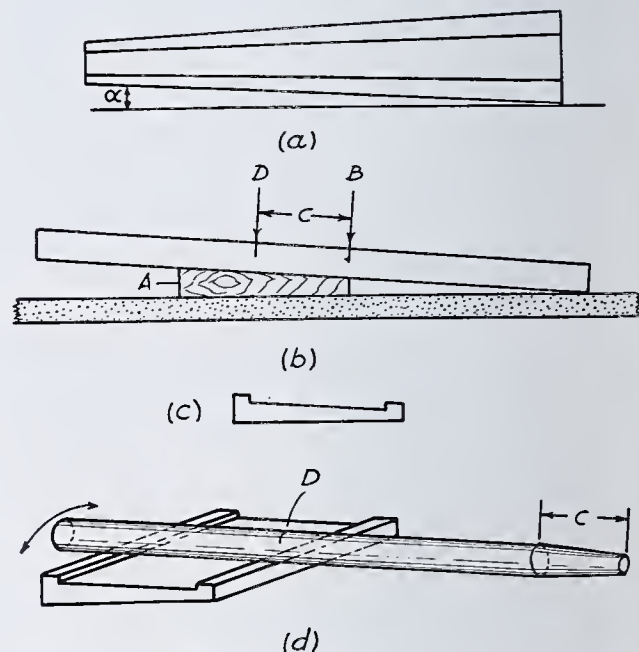


FIGURE 2. WEDGE AND METHOD OF FORMING INNER CONE OF TAPERED JOINT

A good fit may be obtained by a very simple procedure. The outer cone is made in the usual manner, using shapers made from arc carbons or purchased from one of the scientific houses. It is wise to lubricate the shapers with beeswax, which also prevents them from burning. The inner cone is formed by softening the end of a piece of tubing and then rolling it into shape on a flat surface, supporting the tube at an angle to the surface by the use of an appropriate wedge, such as *A* in Figure 2, *b*. Theoretically, for a perfect fit between the two cones, the small angle of the wedge should be equal to angle  $\alpha$  of *a*. Actually, an angle somewhat greater makes the grinding operation easier.

Wood is a satisfactory material for the wedge, which can be cut in any convenient manner. It is suggested that the cross section be made in the shape shown in Figure 2, *c*. The rail effect minimizes the tendency of the tube to twist while being rolled. A wedge 10 cm. long, 4 cm. wide, and 6.5 and 4 mm. high on the high and low sides, respectively, is suitable for tubing up to 15 mm. in diameter. For larger tubing a wedge with double the dimensions is convenient.

No other accessories are needed. The wedge is placed on a clean, smooth, refractory surface, such as the Transite top of a glass-blowing bench. The desired tubing is placed on the wedge with the end just touching the Transite, in the position shown in *b*. The edge of the wedge is marked with a wax pencil, at *B*. If the desired length of joint is *C*, then another mark, *D*, is made on the tube at distance *C* from *B*. By guiding *D* along the edge of the wedge in the rolling operation, the cone is made the correct length (Figure 2, *d*). The end of the tube is heated to the softening point in the blast lamp flame and then the tube is rolled back and forth on the wedge with the palm of the hand, following the guide line with the index as described above. It is usually necessary to reheat the glass several times. The tendency of the tube to thicken during the rolling operation can be lessened



by giving it a preliminary draw to start the taper and then continuing as described above.

By this method a 10-mm. joint may be shaped and ground in about 15 minutes of actual working time.

### Rubber Tape

A very convenient material, both in glass blowing and in the general laboratory, is ordinary electricians' rubber tape. It is extremely cohesive, being made of uncured rubber stock. One of its

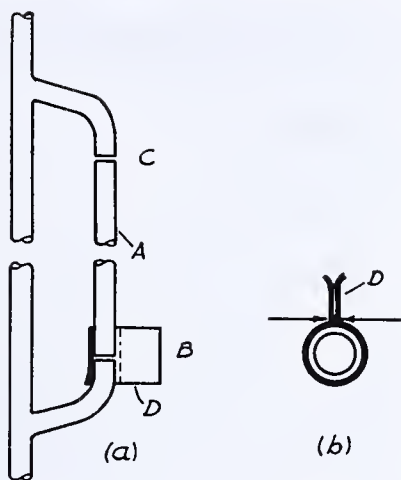


FIGURE 3. USE OF RUBBER TAPE

uses is illustrated in Figure 3, *a*. When sealing a section of the tubing, *A*, into an apparatus an air-tight, flexible joint may be made at *B* with a single turn of rubber tape which is butted together and pinched with the finger tips as in *b*. After the seal at *C* is made, the tape is torn off by grasping the tab, *D*.

Most irregular joints may be sealed by stretching the tape as it is wrapped around the joint. Several turns will seal a stopper in an irregular tube. A convenient temporary repair in a vacuum system may be made by using a technic described by DuMond and Youtz (1) and attributed to Lauritsen and Crane. The organic chemist should find it useful for numberless purposes.

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## Filling Closed-End Mercury Manometers

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A NUMBER of methods have been proposed for filling closed-end mercury manometers without boiling out the mercury inside the manometer (1, 2, 3, 5). However, these methods, although avoiding the difficulties and inconveniences encountered in boiling out the mercury inside the manometer, are either complex in setup or give impure mercury because of contact with grease. In order to circumvent these difficulties, various manometers, such as that of Zimmerli (6), have been devised which do not have to be filled by boiling out, but in general they suffer from being large and unwieldy or difficult for the inexperienced glass blower to make.

By means of a modification of the method proposed by Malmberg and Nicholas for periodically boiling out entrapped gases from the oil in an oil manometer (4), closed-end mercury manometers may be very easily filled. The method is extremely simple and may be used by beginning students on soft-glass manometers, or may be modified to take care of filling more complex manometers, where an all-glass system is desired. Its greatest use probably lies in filling simple manometers for general organic work.

The only equipment necessary is a good Hyvac pump and a bulb (or a wide tube constricted at both ends) large enough to hold in its lower portion all the mercury necessary to fill the U-tube, as shown in Figure 1. The bulb containing the mercury, which should be dry and pure, is attached with pressure tubing to the open end of the manometer and to the Hyvac pump. When the maximum vacuum is attained, the air is driven out from between the glass and the mercury by shaking and tapping. The manometer and mercury may then be gently heated to drive out all volatile matter. When all the air is out, the mercury is carefully poured down into the U-tube and air is let in slowly to fill the manometer.

This method may be modified for more complicated types of mercury manometers. For a manometer containing a stopcock the above method may be used or else a bulb may be sealed on between the stopcock and the U-tube, as shown in Figure 2. The mercury in the bulb may then be heated gently to expel the air, the U-tube filled, and the bulb pulled off in

the torch. This arrangement prevents the mercury from coming into contact with stopcock grease. In the case of a sloping manometer (1), a bulb may be sealed on temporarily and the outfit attached to a mercury diffusion pump. The manometer is then baked out while the mercury is heated, and the mercury is then distilled into the cooled manometer.

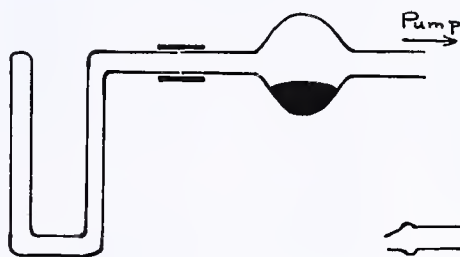


FIGURE 1

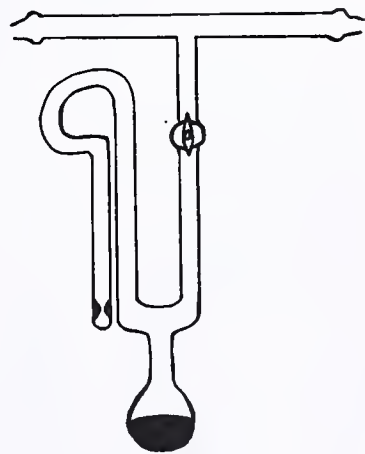


FIGURE 2

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RECEIVED August 10, 1938.



# Absorption Efficiency of Spiral Gas-Lift Wash Bottle

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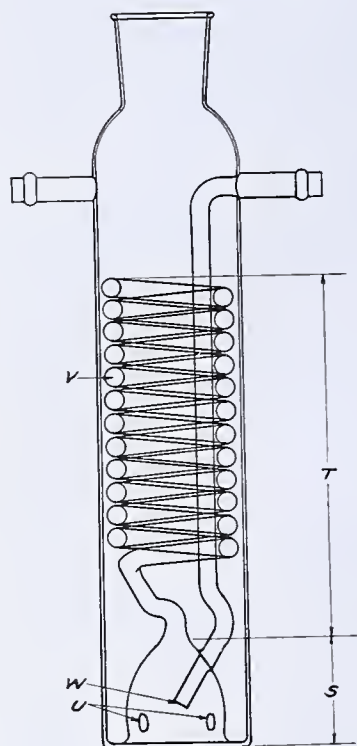


FIGURE 1

THE wash bottle shown in Figure 1, which has been found to be a useful laboratory tool, is similar to absorbers described by Weaver and Edwards (7), Keller (2), Milligan (5), Friedrichs (1), Martin and Green (4), Shaw (6), and Martin (3). It gives intimate and prolonged contact between gas and liquid with recirculation and economy of liquid reagent. The ratio of gas to liquid in the mixture being pumped through the spiral can be varied by changing the liquid level.

This bottle is especially suitable for scrubbing gas with the 2-phase liquid system of bromine and water. The gas pumps alternate slugs of bromine and water up the spiral and out the top,

where the bromine falls through the water to the bottom of the bottle and is immediately recirculated. Consequently, not only is the gas thoroughly scrubbed by the bromine water but the water is continuously in contact with bromine. The Friedrich bottle, on the other hand, allows the bromine layer to remain more or less stagnant at the bottom of the bottle, and consequently the water is not continuously maintained saturated with respect to bromine.

The bottle can be made in different sizes, but a certain relationship must hold between lengths  $S$  and  $T$  to keep the gas from short-circuiting through holes  $U$  rather than passing up spiral  $V$ . In the usual bottle,  $S$  is 60 mm.,  $T$  is 80 mm., and the spiral consists of 11 turns of tubing 6 mm. in outside diameter (3.8 mm. in inside diameter). The volume capacity of the spiral is 11 cc. The gas delivery tube is constricted at  $W$  to about 3-mm. inside diameter. The outer shell of the bottle is about 40 mm. in outside diameter. Alternate slugs of gas and liquid ascend the spiral and are in contact over a length of 950 mm. The back pressure, however, is no greater than that of an ordinary bottle of the Drechsel type when the length of contact between gas and liquid is only about 50 mm.

## Experimental

At first it was thought that the contacting efficiencies could be compared on the basis of the amount of water removed by a stream of gas. However, this method was not applicable because of the disturbing influence of entrainment.

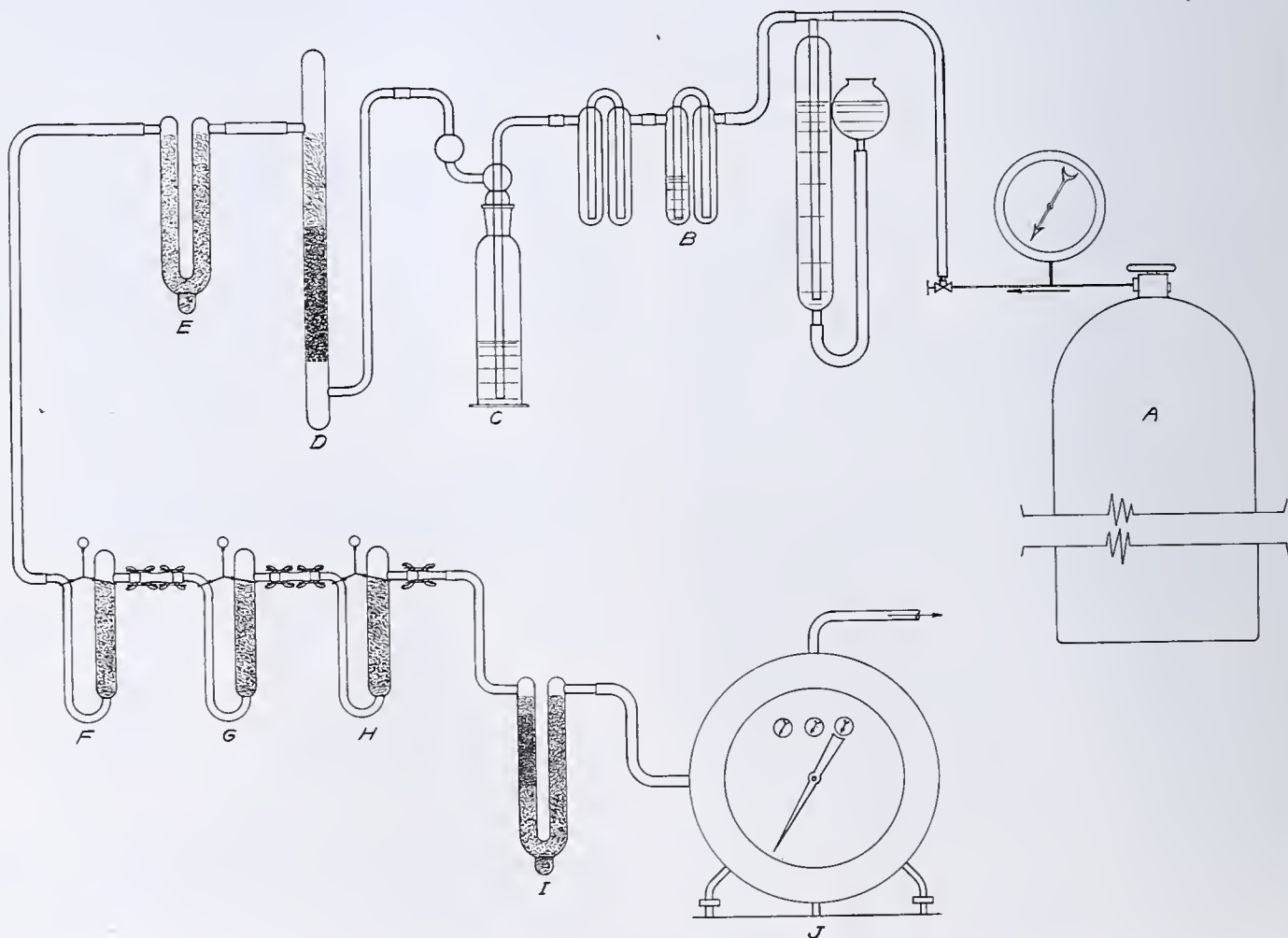


FIGURE 2



With the spiral bottle, the amounts of water removed per liter of nitrogen at the gas rates of 0.6, 1.4, 2.8, 5.6, 9.9, and 15.3 liters per hour were 0.0177, 0.0187, 0.0180, 0.0173, 0.0173, and 0.0173 gram, respectively. With the Drechsel bottle, the amounts removed at the same gas rates were 0.0177, 0.0172, 0.0169, 0.0175, 0.0184, and 0.0185 gram, respectively. The saturator temperature was 20° C., the pressure within the saturator was 754 mm., and the volume of the nitrogen was converted to 20° and 760 mm. The theoretical amount of water was 0.0178 gram.

TABLE I. ABSORPTION EFFICIENCIES AT CONSTANT GAS RATE AND DIFFERENT CAUSTIC CONCENTRATIONS

Weight % KOH	Total CO <sub>2</sub> Passed		Unabsorbed CO <sub>2</sub>		Efficiency	
	Drechsel Grams	Spiral Grams	Drechsel Gram	Spiral Gram	Drechsel %	Spiral %
15	1.096	1.119	0.0419	0.0010	96.2	99.9
5	1.200	1.114	0.1161	0.0018	90.3	99.9
4	1.119	1.105	0.1399	0.0015	87.5	99.9
3	1.132	1.115	0.2042	0.0143	82.0	98.7
2	1.119	1.119	0.4263	0.2093	61.9	81.3

The following method was finally adopted: A mixture of about 99 per cent of nitrogen and 1 per cent of carbon dioxide was passed through 100 cc. of caustic in the bottle being tested and the weight of carbon dioxide escaping absorption was determined. The setup is shown in Figure 2. The gas in cylinder A was passed at constant rate through bubble-counter B into the caustic in bottle C. The exit gas from C was dried by calcium chloride D and by Anhydron E, and the carbon dioxide was absorbed by Ascarite F and G. The water vapor from the Ascarite was retained by Anhydron H, whence the gas passed through protector tube I containing Anhydron, Ascarite, and calcium chloride, and finally through meter J.

The absorption tubes were weighed against a counterpoise with the usual precautions. Anhydron H was necessitated by the vapor pressure of Ascarite. The average weight increase of Anhydron H was 0.0098 gram, corresponding to a vapor pressure for Ascarite of 0.16 mm., which is significant when large volumes of gas are involved.

Table I presents data on the relative efficiencies of the two bottles, using different concentrations of caustic. The nitrogen-carbon dioxide mixture contained 0.01736 gram of carbon dioxide per liter of nitrogen (20° C., 760 mm.). The gas rate was 3.8 liters per hour and approximately the same volume of gas was passed in each experiment (63.5 liters of exit nitrogen; 20° C., 760 mm.). Volume of caustic was 100 cc. in each run.

TABLE II. ABSORPTION EFFICIENCIES WITH 4 PER CENT POTASSIUM HYDROXIDE AT DIFFERENT GAS RATES

Gas Rate Liters/hr.	Total CO <sub>2</sub> Passed		Unabsorbed CO <sub>2</sub>		Efficiency	
	Drechsel Grams	Spiral Grams	Drechsel Gram	Spiral Gram	Drechsel %	Spiral %
3.8	1.119	1.105	0.1399	0.0015	87.5	99.9
7.6	1.228	1.243	0.1830	0.0050	85.1	99.6
11.5	1.228	1.226	0.2033	0.0072	83.4	99.4

Table II presents data on absorption efficiencies at the same concentration of caustic but with different gas rates. The nitrogen-carbon dioxide mixture used at the gas rates of 7.6 and 11.5 liters per hour contained 0.01943 gram of carbon dioxide per liter of nitrogen (20° C., 760 mm.).

Acknowledgment

The authors express thanks to F. L. Hayes for the glass blowing and to William Cerveny for analytical work.

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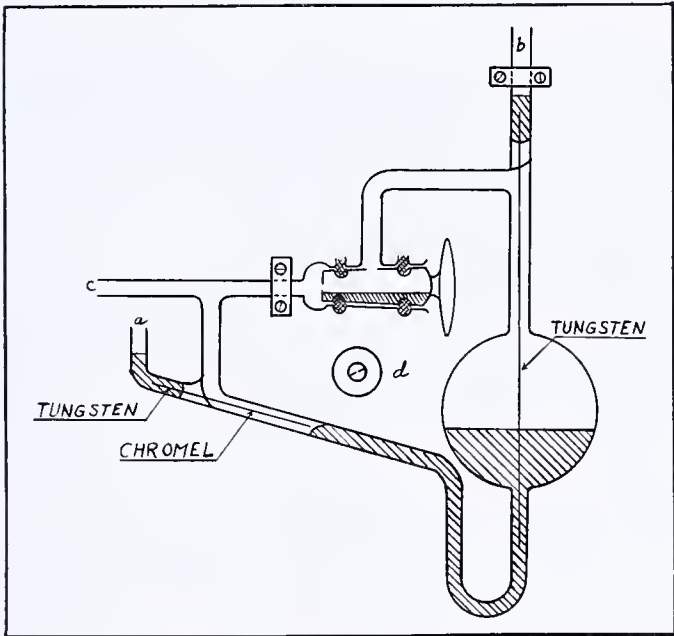
RECEIVED July 24, 1938.

Improved Vacuum Regulator

CLAYTON W. FERRY

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OF THE several devices designed to maintain a constant pressure for vacuum distillation, that described by Ellis (1) has proved to be the most satisfactory. However, at pressures of 3 mm. or less, even the small variations in pressure that this regulator allows cause appreciable changes in the boiling point of materials being distilled, and some distillations tend to build up pressures in the portion of the system beyond the capillary. This capillary, while equalizing and smoothing out variations in pressure caused by the intermittent operation of the pump, also slows up the evacuation of the distillation system, occasionally causing a lag after the distillation is started.



The first of these objections can be overcome by tilting the arm of the regulator, in which contact between the mercury and the electrode is made, from vertical to almost horizontal, as is shown in the accompanying sketch. This causes the meniscus to travel a greater distance per unit change in pressure. Tubing 4 to 5 mm. in inside diameter is small enough to decrease any tendency of the mercury column to oscillate. If larger tubing is used, it is advisable to put a constriction in the bottom of the U-shaped portion. The mercury terminals for the wires leading to the relay are designated by a and b, while c leads to the pump and d is a pivot for the mounting board.

As mercury tends to stick to the platinum or tungsten wires generally used for these contact electrodes, thus reducing the sensitivity, it was necessary to use Chromel wire for the actual contact. To facilitate the making of a good glass seal, the Chromel wire was soldered to a piece of tungsten wire, which was in turn sealed into the side arm. A condenser across the electrodes of the regulator reduces sparking and prevents fouling of the Chromel contact.

To operate, evacuate with the stopcock open until approximately the desired pressure is reached, close the stopcock and make the fine adjustment by tilting the assembly board on its pivot as described by Ellis. The base of a Bunsen



burner, or better yet a Hoke valve, makes an easily adjustable bleeder in the system to keep the pump operating at reasonable intervals.

With this arrangement, the capillary between the two reservoir bottles (1) can be removed entirely, and pressures below 30 mm. are so constant that no variation can be detected on a manometer read with a reading glass. For pressures much above this value, there is a minute variation due to the effect of the extra stroke of the pump after the circuit is broken. If the same absolute constancy of pressure is desired at these higher levels, it is necessary to use a large

reservoir system or resort to an arrangement in which the pump runs continuously, a glass capillary bleeder of the proper capacity being opened and closed by means of a rubber cap on the relay arm.

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RECEIVED March 18, 1938. This device was developed in the course of work done at The Johns Hopkins University under the John M. Hancock Fellowship for North Dakota.

## A Small Low-Temperature Rectifying Column

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THERE is frequently a need for a small low-temperature column, which can be readily moved from place to place in the laboratory and does not require elaborate pressure or temperature controls or a vacuum system for its operation. Small quantities of gases are often generated in chemical reactions, and such a fractionating device would be of value for their purification and determination.

Figure 1 shows a design of such a column. It has a capacity of about 5 cc. of liquefied gas, is small enough to fit into the usual commercial 0.95-liter (1-quart) vacuum flask, is secured on a laboratory ring stand and so is readily portable, and requires for its operation only the addition of a potentiometer for temperature measurements, a source of electric current for a small heater that may be dry cells or a 110-volt line with rheostats, and an ordinary laboratory water-suction pump.

*K* is the liquid container with a volume of about 5 cc. This contains a protruding nipple, *L*, wound with a heating coil of asbestos-covered Nichrome wire, B. & S. No. 26. In this nipple is a reëntering thermocouple tube containing a copper-constantan couple. In the column section, *J*, glass-ring packing, held in place by a small cross bar, is contained in an inner tube of about 9-mm. outside-diameter with a dropping tip on the end. The condenser, *H*, consists of three concentric tubes: The innermost is of 0.47-cm. (0.19-inch) copper tubing, the middle is of 11-mm. glass, the closed lower end of which terminates in a dropping tip, and the outside tube is 20 mm. in diameter. At the lower end of the condenser a 7-mm. take-off tube, *I*, enters through the wall. Into this a reëntering thermocouple tube carries a copper-constantan couple. The liquid-air reservoir above the condenser is double-walled and contains a center tube, *F*, through which extends the copper tube, *G*. *G* is notched at the top to allow free access of air and is held in place by a small rubber ring. A glass bell, *E*, rests on the top of *G*. A board fastened to the

top of the liquid-air reservoir holds the entire device, and to it are fastened the necessary stopcocks and terminal binding posts (not shown in the diagram). The column fits into a quart-size Pyrex glass unsilvered vacuum flask, *M*, which is surrounded by a radiation shield, *N*, of aluminum sheet containing slots cut into it for observation of the important parts of the column. The tubes to the stopcocks are 5 mm. in outside diameter.

In operation *J* and *K* are first used as a trap to receive the material to be distilled. With *M* removed and *J* and *K* immersed in liquid air or other suitable condensing medium, the gas is admitted through stopcock *D*, with stopcock *B* open to permit escape of air. Flask *M*, which has been chilled with liquid air but is empty, is then replaced, *D* is closed, and *C* is connected to a water-suction pump. Two glass traps to act as receivers are connected with rubber tubing to the two outlets of the three-way stopcock, *A*, and are immersed in vacuum flasks containing suitable condensing medium. Liquid air is placed in the reservoir, and air is drawn into the condenser when *C* is opened. This air is both dehydrated and cooled as it is forced to travel over the surface of the liquid air, and it cools the condenser. The amount of cooling can be regulated by the volume of air admitted. When the condenser is cold, heat is supplied with *A* closed and *B* open. Observation enables adjustments to be made until reflux is obtained and equilibrium established. *B* is then closed and *A* opened to one of the receivers. The amount of take-off can be regulated by adjustments of both the amount of heat supplied to the pot and cooling supplied to the condenser. Temperatures of both the pot and top of the column can be obtained by a potentiometer, and receivers can be changed at will.

This device is a total condensation column operating at constant pressure. The receiving traps must, therefore, be open to the atmosphere. A column of this design has been used successfully with liquids boiling at  $-130^{\circ}$ ,  $-80^{\circ}$ , and  $-50^{\circ}$  C.

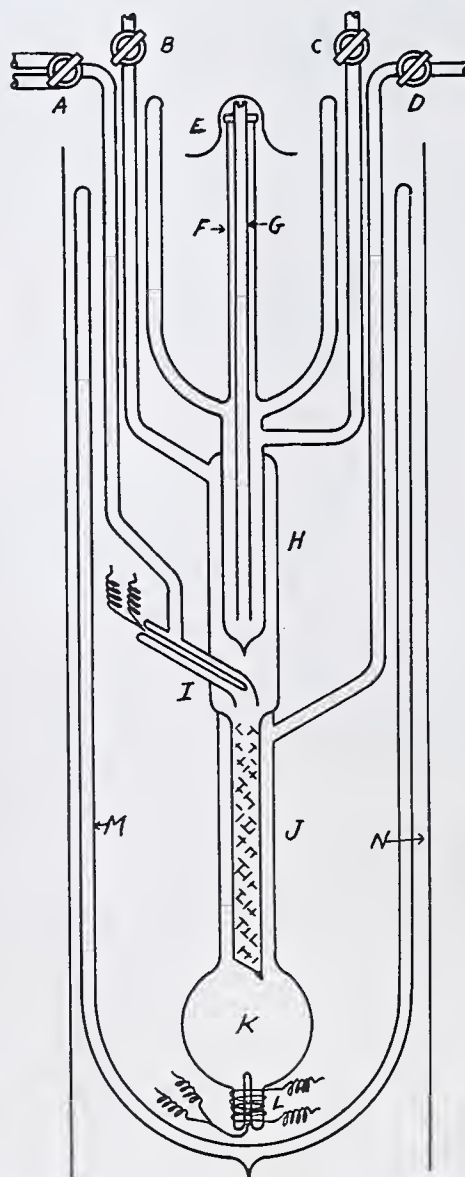


FIGURE 1

RECEIVED July 26, 1938.





# Modern

# Laboratories

## Hooker Electrochemical Company Research Office Building

G. F. RUGAR, Hooker Electrochemical Company, Niagara Falls, N. Y.

THE Hooker Electrochemical Company, Niagara Falls, N. Y., has recently finished the construction of a three-story office building for the use of the Research and Development Department. The need for such a building has long been recognized because of crowded conditions in the Main Office Building which also housed the Operation and Engineering Departments. It had been desirable, also, to get the Development and Research Department staff near the Research Laboratories in order to make for greater efficiency in the department as a whole.

A great deal of careful planning was done in connection with the architecture and appearance of this building, which is the first of a series of buildings which will extend along Buffalo Avenue as the company expands and creates the need for them. Both the interior and the exterior are so arranged that additions may be made at either end and preserve a pleasing architectural appearance.

The new building has the form of a T-shaped addition to the Research Laboratory Building, with which it forms an H. The new building is of brick and stone construction with segmental arch windows carrying up through two floors and with machicolated cornices. A short flight of stone steps leads from the street into the entrance vestibule on the first floor. The vestibule opens into a corridor from which all offices on this floor and also the stairs leading to the ground and second floors may be reached. All ceilings are finished with an acoustic material to deaden sound. Indirect lighting is used in all offices, while direct lighting is used in the laboratory. Air conditioning is provided the year round. All air ducts, water pipes, and electric conduits are carried in the false ceilings of the corridors. Telephone wiring is concealed in fiber ducts in the floors and connections are made to brass outlets which are located inconspicuously under desks or tables. Floors are of asphalt tile in a two-tone effect.

The entire west end of the second floor is taken up with a library, while the balance of this floor is given over

to offices. The library is equipped with open stacks of adjustable steel shelves on all of the free space of the walls. All other furniture in the library, including card index files, magazine rack, dictionary stand, tables, and chairs, is of either steel or aluminum.

The shape of the buildings has made necessary some variation in the size of offices. Five large offices, one on the second floor and two on each of the other floors, are normally occupied by only one person, but are spacious enough to be used for conferences. Each has a permanently installed blackboard which is cleverly concealed by a Venetian blind when not in use. Except for the vestibule, the entire first floor is taken up with offices.

### Laboratory

On the ground floor are offices, storage room, heating and air-conditioning equipment room, and an excellently equipped analytical laboratory. The importance of accurate work in a research program is clearly indicated in this laboratory.



HOOKER ELECTROCHEMICAL CO. RESEARCH AND DEVELOPMENT DEPARTMENTS



Probably more thought was put on the planning of the laboratory than any other room in the building. It is  $30 \times 18$  feet and occupies the entire west half of the bar of the H. The tables, hoods, and storage cabinets are constructed of copper-bearing, lead-coated steel, finished in aluminum.

At the left of the door and at the one end of the room is an electric refrigerator for storage of inflammable liquids, which is also used for general cooling purposes. Beyond this are the tables for balances.

A table runs along the full length of the outside wall. For a space of 11 feet this table is 30 inches high and the remainder is 36 inches high. The section of the table of lower height was designed for titration work with the operator seated in a comfortable laboratory type of chair. Underneath this table and enclosed behind solid cupboard doors are stock solutions of analytical reagents contained in 5-gallon bottles. These bottles are connected to the compressed air system, so that the solutions may be forced up glass tubes running through the top of the table and delivering into the tops of burets. An obvious advantage of this arrangement is that all solutions are protected from the light.

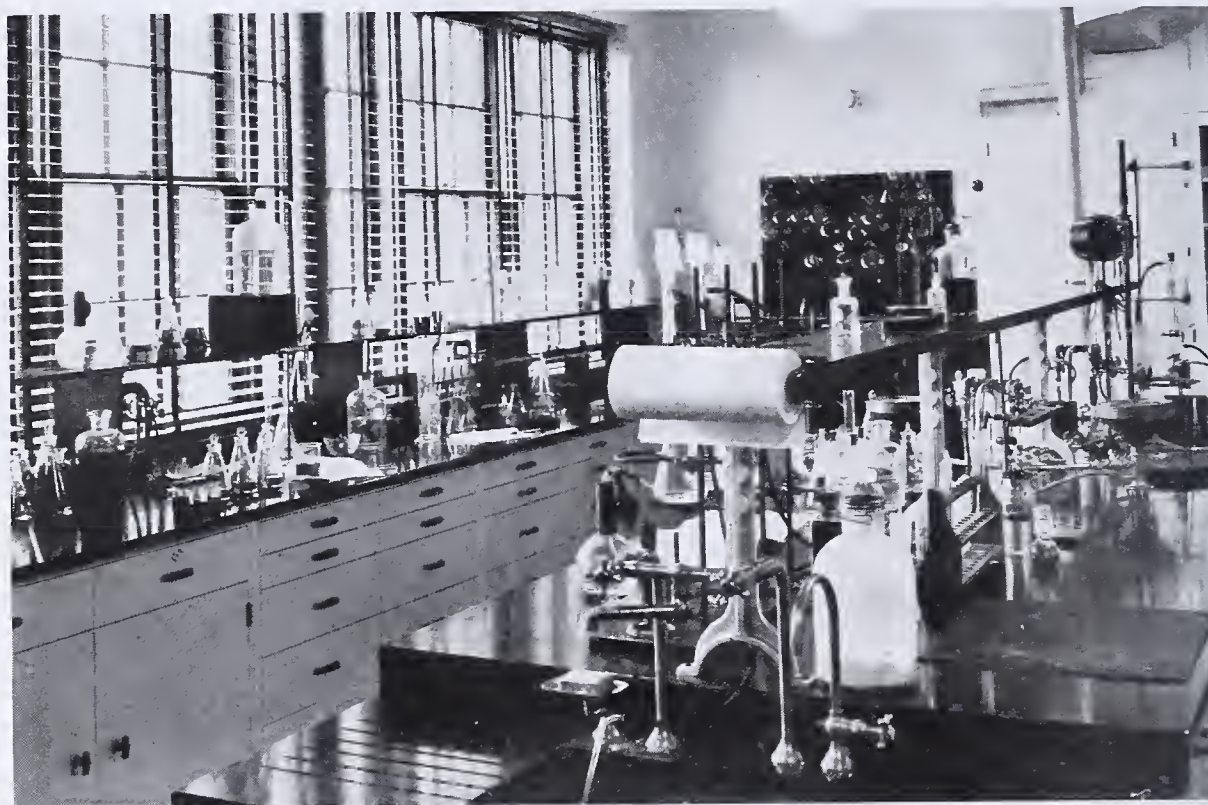
At the far end of the room is a sink and drain board unit which is made of one piece of Karcite. Adjoining the sink are two storage cabinets, one with solid doors for chemicals and the other with glass doors for glassware.

The fourth side of the room is taken up with a fume hood and a table for muffle furnaces and electric ovens. The fume hood is divided into two sections, one 4 feet long fitted with a steam bath and the other 8 feet long. Both hoods are vented to the roof of the adjoining building.

The center table is of the conventional type with working space on both sides, drawer and cupboard space underneath, and a large sink at one end.

All tables are provided with adequate numbers of gas, compressed air, electric, steam, and water outlets. All piping to the tables and hoods is concealed beneath them. Receptacles for refuse are out of sight under the sinks and openings to them are provided through the sheet-metal panels. A metal desk and chair and a metal wardrobe storage cabinet are the final items of equipment.

The building has now been occupied for some months and has worked out admirably in every respect.



(Left)  
RESEARCH  
ANALYTICAL  
LABORATORY



(Below)  
LIBRARY





# Microchemistry

## Sulfate Titration

### Use of Tetrahydroxyquinone in a Semimicromethod

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Valentine's Meat-Juice Co., Richmond, Va.

A RAPID semimicro sulfate method was needed in this laboratory. With colored unknowns containing organic matter, considerable difficulty was experienced in direct titration of sulfate with tetrahydroxyquinone used internally as recommended. Sharp end points were essential in order to estimate sulfate ion in the range of 3 to 6 mg. contained in 0.1 to 1.0 ml. of original sample. Although the pale, yellow-brown color in most of the samples as diluted for titration was not so intense as to cause difficulty, a method useful in the presence of considerable color was preferred for more general application. The unknowns (liver extract fractions) had pH values of 5.8 to 6.8 and contained 14 to 35 per cent weight by volume of organic matter, as well as small but undetermined amounts of phosphates. Highly accurate results for sulfate were not expected in these particular direct titrations, but reproducible comparative results were required to follow the course of sulfate removal. The samples, as a rule, were left unneutralized to diminish the possibility of high results caused by phosphate and organic constituents, such as nucleic acids.

The end point was less indefinite with the newer tetrahydroxyquinone (organic dispersing agent) described by Sheen and Kahler (3), but still indeterminate over a range of 0.1 ml. in titration of the above unknowns. Winsor (4) had described the successful use of 2-methoxyethanol (methyl Cello-solve, supplied by the Carbide and Carbon Chemicals Corp.) as a color stabilizer in the ferric thiocyanate reaction. While the same theoretical considerations did not appear to apply to the barium-tetrahydroxyquinone problem, the possibilities of 2-methoxyethanol were investigated.

Use of the methoxyethanol to replace part or all of the alcohol in the titration medium did not prove an advantage. However, the stability of an aqueous solution of the indicator was markedly increased by inclusion of sufficient methoxyethanol. This indicator solution proved admirable as an outside indicator and permitted adaptation of the method to the authors' needs. Ethanol also impeded indicator fading but was less effective than the methoxyethanol. A compromise was necessary between the proportion of methoxyethanol needed for stability and the proportion of water needed for sufficient color intensity. The solution described below is still usable after 18 hours, although the indicator will have faded somewhat, while a purely aqueous solution is useless after a few minutes.

The general principles and procedure for the macromethod

have been described previously (1, 2, 3). The modifications found desirable for the semimicro scale are included below.

#### Semimicromethod

**SPECIAL APPARATUS.** A semimicroburet—the Koch calcium pipet, provided with a 50-ml. reservoir and a 2-ml. column graduated to 0.01 ml.

**SOLUTIONS.** Indicator: 1 measuring cup (about 150 mg.) of tetrahydroxyquinone preparation (THQ Betz), dissolved in 1.0 ml. of distilled water and diluted with 2 ml. of 2-methoxyethanol.

Titration solution, approximately 0.1 N barium chloride, standardized preferably by titration against about 0.1 N standard sulfuric acid (or neutral sulfate) solution, standardized gravimetrically.

TABLE I. SULFATE TITRATION

Sample	ML.	Total BaCl <sub>2</sub> (Less 0.02- Ml. Blank)	SO <sub>4</sub> of Undiluted Sample, Based on Final BaCl <sub>2</sub> Standardization	
			Gravimetrically Mg./ml.	Volumetrically Mg./ml.
Approximately 0.1 N SO <sub>4</sub>				
Inside THQ	1	1.24+	4.80+	4.92+
Outside THQ	1	1.24	4.80	4.92
Gravimetric	10	..		4.923
Exactly 0.1 N (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>				
Outside THQ	0.5	0.60	4.64	4.76
Outside THQ	1	1.22	4.72	4.84
Outside THQ	2	2.46	4.76	4.88
With 2 ml. additional alcohol	2	2.46+	4.76+	4.88+
Like preceding sample, except no alcohol used	2	2.46	4.76	4.88
Actually present in 0.1000 N salt	..	..		4.803
Liver extract fraction, diluted sixfold				
Outside THQ	1	1.56	36.2	37.2
Gravimetric	12	..		37.6

**STANDARDIZATION.** Description of the standardization procedure essentially outlines the method. The barium chloride solution is standardized conveniently by titration against 1 ml. of 0.1 N sulfuric acid accurately measured with an Ostwald pipet into a 50-ml. beaker. After neutralization with 0.1 N sodium hydroxide and addition of 2 ml. of ethanol, the barium chloride is added from the Koch pipet. As the end point is approached, samples of the well-stirred mixture are transferred (at 0.01-ml. titration intervals) with a small glass rod to droplets of the indicator solution on a suitable spot plate until a droplet turns definitely pink almost immediately. Under these conditions, a blank of 0.01 to 0.02 ml. is deducted. The approximate end point is previously estimated, or, in the case of unknowns, is determined by preliminary titration. Thus, only 3 to 5 droplets need be removed from a total volume of approximately 5 ml., just before the end point is reached in the final titrations. Even with the inclusion of preliminary titrations, a marked economy in tetrahydroxyquinone is effected as compared with internal use of the indicator.



Each titration figure in Table I was obtained from two or more titrations differing by 0.02 ml. or less. The tabulated results show that outside and inside indicators give identical values with a pure sulfate. Apparently these slightly low results tend to be compensated by titrimetric standardization of the barium chloride solution. This is to be expected, with unknowns of equivalent sulfate-ion concentration, as the effect of probable slight incompleteness of barium sulfate precipitation in the course of a rapid titration is canceled out. For highest accuracy, the best procedure appears to be standardization of the barium chloride by titration, coupled with dilution of the original sample to permit use of volumes and sulfate concentrations closely similar to those used in standardization. The results with ammonium sulfate, and other observations, do not entirely convince the authors that addition of alcohol is essential in titrations of this order. Reliable figures for inside indicator titration of liver extract fractions were not obtained because of the indeterminate end points previously mentioned.

The tolerance for phosphate ion unfortunately could not be

raised by the outside indicator method appreciably above the 60 p. p. m. limit determined by Sheen and Kahler (2). Numerous buffers were tried, but the shifting or indeterminate nature of the end points, caused by changes in pH and different buffer systems or concentrations in the presence of phosphates, indicated the impracticability of these procedures.

### Summary

A new and economical tetrahydroxyquinone indicator solution is described which, used externally, greatly facilitates the direct titration of small amounts of sulfate ion in certain unashed samples containing organic constituents.

The interference of phosphate ion is again pointed out.

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## Determination of Small Amounts of Potassium

### A Simpler and More Rapid Variation of the Sodium Cobaltinitrite Method

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THE procedure herein described for the determination of potassium by precipitation with sodium cobaltinitrite is simpler and more rapid than any of the many similar procedures which have been proposed since the original work of Adie and Wood (1). The potassium is precipitated in a relatively short time at room temperature. A centrifuge is used to separate the precipitate, as in the procedures of Kramer and Tisdall (7) and others (5, 8, 9), and obviates the filtration employed elsewhere (1-4, 11, 13). The precipitate is washed only once, whereas two or more washings are required in other procedures (1, 2, 3, 5-9, 11, 13).

The use of ceric sulfate (4) instead of potassium permanganate for the determination of the nitrites in the precipitate is advantageous. The end point with ceric sulfate is very sharp. When potassium permanganate is used, often a precipitate of hydrated manganese dioxide is formed, which necessitates the addition of an excess of sodium oxalate to effect its solution, after which the end point is reached by an additional titration with permanganate. This difficulty is, of course, not encountered when ceric sulfate is used. The procedure is satisfactory for the determination of potassium in amounts ranging from 0.2 to 1.0 mg., the error, in general, not exceeding 2 per cent. It is especially applicable to the determination of potassium in plant material and in soil extracts.

### Reagents

**Precipitating Reagent.** Mix together 46.2 grams of sodium cobaltinitrite, 18.9 grams of sodium acetate, 120.0 ml. of distilled water, and 18.0 ml. of glacial acetic acid. Prepare this solution 48 hours before using. Keep stoppered and in a cold, dark place. Before using, centrifuge to remove any precipitate.

**Ethyl Alcohol.** 95 and 70 per cent by volume.

**Ceric Sulfate.** Dissolve about 9 grams of anhydrous ceric sulfate in 500 ml. of distilled water to which have been added 30 ml. of concentrated sulfuric acid. Make up to 1 liter. This solution, which is approximately 0.02 N, may be standardized with sodium oxalate.

**Ferrous Ammonium Sulfate.** Dissolve 8 grams of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  in 500 ml. of distilled water to which have been added 10 ml. of concentrated sulfuric acid and make up to 1 liter.

**Sulfuric Acid.** Concentrated sulfuric acid diluted 1 to 1.

**Indicator.** 0.025 M *o*-phenanthroline ferrous complex.

### Procedure

To 1.5 ml. of 95 per cent ethyl alcohol in a 15-ml. centrifuge tube add a 5-ml. aliquot of the potassium solution. Mix thoroughly. Add dropwise, with continuous shaking, 2.0 ml. of the precipitating reagent. Allow to stand for 1 hour at a temperature of from 20° to 25° C. Centrifuge for about 10 minutes at about 2000 r. p. m., so that the precipitate is firmly packed in the bottom of the tube. Pour off the supernatant liquid and allow the tube to drain for about 5 minutes. Wash the precipitate with 5 ml. of 70 per cent alcohol, breaking up the bulk of the precipitate by forcing the wash solution in a fine stream from a pipet. Centrifuge for 5 minutes and drain as before. Dry the precipitate for 0.5 hour at 80° to 85° C. to remove all the alcohol.

Add 5 ml. of the ceric sulfate reagent and 1 ml. of 1 to 1 sulfuric acid. Heat in a water bath at 90° to 100° C. until all the precipitate is oxidized, as indicated by its disappearance (usually within about 5 minutes). Maintain an excess of ceric sulfate throughout the reaction (5 ml. of 0.02 N ceric sulfate are sufficient for precipitates containing no more than 0.5 mg. of potassium). Cool to room temperature and titrate the excess ceric sulfate with ferrous ammonium sulfate, using one drop of *o*-phenanthroline ferrous complex as indicator. The end point is very sharp, the color of the solution changing from pale blue to red.

**CALCULATION.** Milligrams of K = ml. of  $\text{Ce}(\text{SO}_4)_2$  used in oxidation of the precipitate  $\times$  normality of  $\text{Ce}(\text{SO}_4)_2 \times 6.52$ .

### Discussion

The precipitating reagent is similar in composition to that used by Adie and Wood (1), but is more easily prepared. It involves one solution only, whereas that used in some other procedures (1, 2, 3, 5-8, 11) involves two solutions. Experience has shown that, after its preparation, it is best to let the reagent stand for 2 days before using. The results will be high if it is used too soon after being prepared. There is no deterioration of the reagent within 2 or 3 weeks if



it is kept in a cold, dark place—e. g., a refrigerator. It is advisable, however, to make daily determinations with known potassium solutions—e. g., solutions containing 0.2 and 0.8 mg. of potassium per 5-ml. aliquot as a precautionary check on the reagent, especially if it is more than a week old.

The precipitation can be carried out at room temperature. Piper (11) noted that the temperature during precipitation influences the recovery of potassium, but concluded that, in his procedure, the recovery was satisfactory at room temperature. In other procedures (5, 13), on the other hand, temperatures from 0° to 6° C. are recommended. Average results showing the effect of temperature on the recovery of potassium for this procedure are reported in Table I. The recovery tends to be high at low temperatures and low at high temperatures. It is apparent, however, that the variations are significant only in the recovery of the 0.2 mg. of potassium. Therefore, it is recommended that when determining small amounts of potassium (0.2 and 0.3 mg.) the temperature be maintained at about 20° C. For larger amounts of potassium, recovery will be satisfactory over the ordinary range of fluctuation in room temperature.

TABLE I. EFFECT OF TEMPERATURE ON THE RECOVERY OF POTASSIUM FROM SOLUTIONS OF POTASSIUM SULFATE

Actual Amount of K Mg.	Temperature ° C.	Amount Recovered <sup>a</sup> Mg.	Per Cent Recovered
0.200	0	0.216	108
0.200	18	0.206	103
0.200	20	0.203	102
0.200	25	0.192	96
0.200	30	0.178	89
0.600	0	0.615	103
0.600	18	0.602	100
0.600	20	0.607	101
0.600	25	0.601	100
0.600	30	0.597	100
1.000	0	1.024	102
1.000	18	1.000	100
1.000	20	0.993	99
1.000	25	0.996	100
1.000	30	1.000	100

<sup>a</sup> Average of four determinations.

The variation in the recovery at different temperatures results from a difference in the solubility of the precipitate and from the effect of temperature upon the composition of the precipitate. The proportion of potassium to sodium in the potassium-sodium cobaltinitrite precipitate increases with temperature (11). As the proportion of potassium to sodium increases, the factor used in the calculation must be increased to compensate for the change in composition. The factor 6.52 used in this procedure is satisfactory for room temperatures. A smaller factor would offset the high results at lower temperatures, and conversely, a larger factor, the low results at higher temperatures. The precipitation is more convenient at room temperature, of course, although the sensitivity of the reaction is greater at lower temperatures (12).

One washing of the precipitate with 5 ml. of 70 per cent alcohol is adequate. Table II shows average results in the recovery of potassium from solutions of potassium sulfate when the precipitates were washed with from one to four successive 5-ml. portions of 70 per cent alcohol. The differences are within the limits of experimental error conceded to this procedure and are not significant. There is a considerable saving of time by washing only once.

When an unknown solution is so dilute that a 5-ml. aliquot does not contain at least 0.2 mg. of potassium, it is necessary to concentrate the solution by the evaporation of a larger aliquot. Satisfactory results cannot be obtained with dilute solutions when precipitation is attempted in aliquots larger than 5 ml., even though the amounts of alcohol and reagent are increased in the proportions used for 5 ml. Fair recovery may be secured with 5-ml. aliquots containing more than 1.0 mg., but the most consistent results are obtained with aliquots

containing between 0.2 and 1.0 mg. of potassium. The error, on the average, does not exceed 2 per cent, particularly with the larger amounts of potassium. As might be anticipated, the exact recovery of small amounts (0.2 and 0.3 mg.) is more difficult, resulting occasionally in a greater error which, however, does not exceed 3 per cent.

TABLE II. EFFECT OF NUMBER OF WASHINGS UPON RECOVERY OF POTASSIUM FROM SOLUTIONS OF POTASSIUM SULFATE

(Washed with 5-ml. portions of 70 per cent alcohol)			
Actual Amount of K Mg.	Number of Washings	Amount Recovered <sup>a</sup> Mg.	Per Cent Recovered
0.200	1	0.202	101
0.200	2	0.201	101
0.200	3	0.197	99
0.200	4	0.201	101
0.600	1	0.605	101
0.600	2	0.602	100
0.600	3	0.602	100
0.600	4	0.612	102

<sup>a</sup> Average of three determinations.

Kramer (6) and others (2, 10, 11) have demonstrated that the sodium, calcium, magnesium, barium, strontium, zinc, iron, sulfate, chloride, nitrate, and phosphate ions do not interfere in the volumetric determination of potassium with sodium cobaltinitrite. Similar results have been obtained with this procedure. Ammonia is the only substance which will seriously interfere. In soil extracts ammonia is eliminated from the sample by evaporation and ignition. If there is any danger of contamination from ammonia fumes in the laboratory, the centrifuge tubes should be stoppered during the precipitation. It should be noted, with respect to sodium, that the ratio of sodium to potassium in the reaction mixture influences the composition of the precipitate (14). According to Schueler and Thomas (13), an excess of sodium over potassium gives the best results. Within limits, at least, the reaction of the unknown is unimportant, the recovery of potassium being equally satisfactory from solutions ranging in pH from 1.5 to 12.

TABLE III. EFFECT OF COBALT ON CERIC SULFATE REQUIRED FOR SUBSEQUENT TITRATION

Trial No.	0.021 N Ce(SO <sub>4</sub> ) <sub>2</sub>	
	Cobalt present Ml.	Cobalt absent Ml.
1	3.72	4.14
2	3.68	4.07
3	3.72	4.15
4	3.66	4.11
Av.	3.69	4.12

Ratio 3.69 : 4.12 = 10.8 : 12

The factor 6.52 used in the calculation of the potassium in the precipitate is empirical. It was noted by Drushel (3) and later by others (2, 6, 7, 8, 11) that in the titration of the nitrites in the precipitate the cobalt is reduced, accounting for one equivalent of the nitrites, the other eleven being accounted for by the oxidizing agent (ceric sulfate in this procedure). If the precipitate has the composition K<sub>2</sub>NaCo(NO<sub>2</sub>)<sub>6</sub> as determined by Adie and Wood (1), the stoichiometric factor is 7.10 when the action of the cobalt is considered. However, when the cobalt is not considered and all the twelve nitrite equivalents are accounted for by the ceric sulfate, the stoichiometric factor is 6.52, which is also the factor used in this procedure. Since this indicates that the cobalt might not act in an oxidizing capacity under the conditions of this procedure, analyses were made in which the nitrites in two sets of precipitates containing 0.5 mg. of potassium were titrated, one in the presence of cobalt as usual, and the other in the absence of cobalt which was removed by filtration after being precipitated with sodium hydroxide. The data are shown in Table III.



The average number of milliliters of 0.021 *N* ceric sulfate necessary to oxidize the nitrites in the presence of cobalt was practically eleven-twelfths (10.8/12) of that necessary when cobalt was removed—i. e., the cobalt accounts for the oxidation of one of the twelve nitrite equivalents in the precipitate. This confirms the results of Drushel (3) and others (2, 6, 7, 8, 11) and establishes the factor 6.52 as empirical for a precipitate of the composition  $K_2NaCo(NO_2)_6$ ; its identity with the stoichiometric factor for a precipitate of this composition is merely coincidental. An explanation of the relation may be found in the fact that a variability in the composition of the precipitate between  $KNa_2Co(NO_2)_6$  and  $K_2NaCo(NO_2)_6$  as a result of variations in the conditions of precipitation has been noted by several investigators (8-12, 14). It is possible that the precipitate in this procedure approaches the relative composition  $K_{1.84}Na_{1.16}Co(NO_2)_6$ , which is the approximate formula for which the factor 6.52 is stoichiometric in the presence of cobalt. No analyses have been made of the composition of the precipitate, and the above formula is merely suggested as a possible means of explaining a seemingly empirical relation. Until the actual composition of the precipitate formed in this procedure is determined, the factor 6.52 must be considered as empirical. The procedure is of definite practical importance, especially when applied to soil extracts, and while the nature of the precipitate and the character of the factor are of interest, the practical application of the procedure should not be neglected because of any obscurity as to the theoretical considerations latent in the method.

### Acknowledgment

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## Microscopic Identification of Some Important Substituted Naphthalenesulfonic Acids

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THE commercial importance of the naphthalenesulfonic acids has resulted in numerous methods for the identification of these difficultly characterized compounds.

In most cases their salt-forming properties have been utilized in preparing metallic or arylamine salts (1, 2, 3, 5-8, 10, 12). Chambers and Scherer (4) used the base benzylisothiurea for characterization of  $\alpha$ - and  $\beta$ -naphthalenesulfonic acids and the 1,5-, 1,6-, 2,6-, and 2,7-disulfonic acids. Hann and Keenan (11), using microscopic methods with this reagent, reported the optical data on the derivatives of these same acids. The limitation of the above methods is their lack of applicability to large groups of the acids. By a combination of such procedures—metallic salt formation, benzylisothiurea salts, and free acids—Garner (9) outlined a procedure for the microscopic identification of twenty substituted naphthalenesulfonic acids. His method requires the preparation and examination of a number of derivatives of each acid.

The method which is here reported is based upon the fact that benzoylation of a number of naphthylamine-, naphthol-, and aminonaphtholsulfonic acids yields characteristic, readily isolated test forms.

Photomicrographs of the derivatives and the free acids or their sodium salts are included (all of the same magnification, approximately 70). The latter two are generally poorly described in the literature and are in many cases character-

istic and serve as additional proof of identity. Optical data are given for the derivatives.

### General Procedure

**PURIFICATION OF SAMPLES.** All acids insoluble in water are dissolved in strong sodium carbonate solution and treated with activated carbon (Darco). The free acid precipitated with hydrochloric acid is filtered by suction, washed with a little cold water, reprecipitated similarly a second or third time, and dried at 40° to 50° C. In what follows, unless otherwise noted, this is the purification procedure used.

**PREPARATION OF BENZOYL DERIVATIVES.** For monosubstituted acids—naphthylamine- or naphtholsulfonic acids—0.2 gram of the acid or its sodium salt is dissolved in 10 ml. of approximately normal sodium carbonate solution in a 125-ml. glass-stoppered Erlenmeyer flask and 0.2 ml. of benzoyl chloride (reagent quality) added. With disubstituted acids such as the aminonaphthol type the quantities of sodium carbonate and benzoyl chloride are doubled; otherwise the procedure is the same.

Contrary to usual procedure, sodium carbonate appears to serve better than sodium hydroxide for the benzoylation, the derivative frequently precipitating more easily when the carbonate is used. No trouble is experienced from gaseous carbon dioxide, as it is absorbed in the excess of carbonate used.

The flask is stoppered and vigorously shaken until all odor of benzoyl chloride has disappeared. This may take as long as 5 minutes in some cases and a precipitate may or may not form, depending on the sulfonic acid.



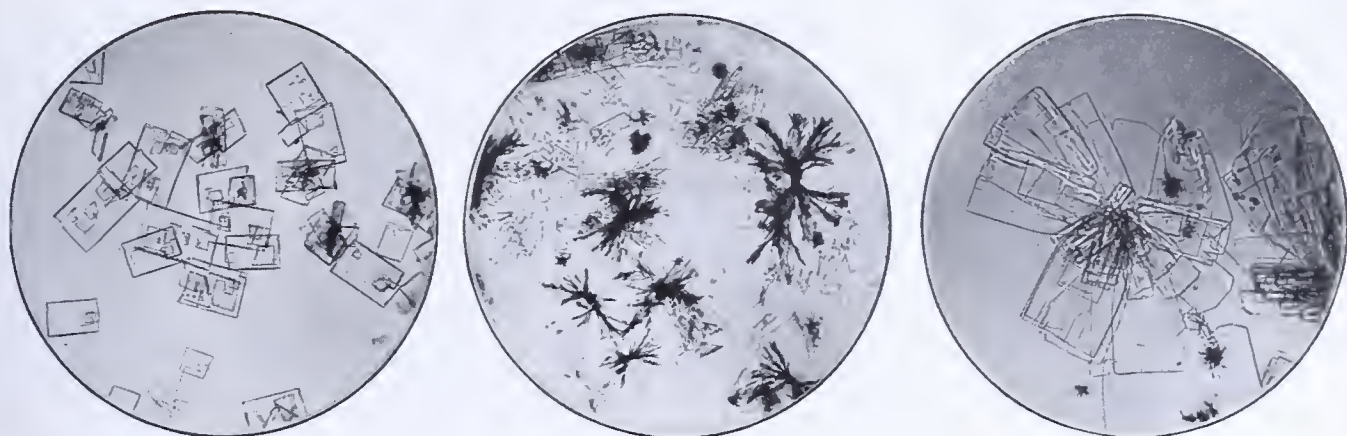


FIGURE 1. 1-NAPHTHYLAMINE-7-SULFONIC ACID (CLEVE'S ACID 1,7)  
Left. Free acid from hot solution      Center. Free acid from cold solution      Right. Benzoyl derivative

If a precipitate forms, it is filtered by suction. Sufficient fine solid c. p. sodium chloride is added to the filtrate to make about a 20 per cent saline solution. If more precipitate forms, it is collected with the original and the filtrate is discarded. This salting-out procedure is necessary only if it is desired to increase the yield; otherwise the original precipitate is used and the filtrate discarded immediately. If no precipitate forms during benzoylation, the above salting-out procedure is applied. Rarely is a concentration of more than 20 per cent of salt required for complete precipitation.

The derivative is removed from the filter and dissolved in 10 ml. of water, warming to 40° C. if necessary to aid solution. A small amount of Darco is added and the solution is filtered, cooled, and salted out as before. This reprecipitation is repeated (eliminating the Darco after the first time) until the filtrate is neutral to phenolphthalein. Usually two or three recrystallizations are sufficient. The precipitate is spread on a porous plate and dried in a desiccator. Oven drying tends to darken the derivatives in some cases.

**RECRYSTALLIZATION OF DERIVATIVES FOR MICROSCOPIC EXAMINATION.** To make the method generally applicable, a standard crystallization technic has been developed and is applied as far as possible. Adherence to this procedure gives consistently reproducible test forms. Appreciable deviations yield unsatisfactory or misleading results. Crystallizations on the slide do not generally permit of sufficient control of conditions.

A 1 per cent solution is made by dissolving 0.02 gram of the dry derivative in 2 ml. of water in a test tube, warming if necessary to effect solution. After cooling to room temperature, fine or powdered c. p. sodium chloride is added in very small amounts (5 mg. at a time), shaking until the portion added has dissolved before adding more. This addition of salt is continued until the solution becomes slightly cloudy, indicating that precipitation of the derivative has begun. The solution is now warmed to redissolve the precipitate and set aside to cool. Crystallization occurs in from 15 minutes to an hour if the salting out has been properly performed.

If precipitated too rapidly—that is, if too much salt is added—no characteristic crystals are obtained but merely an indefinite mass of poorly defined forms. If too little salt is added crystallization is unduly prolonged or does not occur at all.

Under ideal conditions a slight cloud of crystal nuclei appears 5 or 10 minutes after warming, growing in 10 or 20 minutes more to a small amount of crystalline precipitate that settles to the bottom of the tube. A small amount of the precipitated crystals and mother liquor is now transferred to a slide, using a glass tube of about 2-mm. bore. (This size of tube prevents breaking up some of the large spherulites frequently found.) Appearance is the final test of proper precipitation. If indefinite forms are obtained, a new precipitation should be made using less salt.

Any deviations from the above procedure will be noted.

**BENZYLISOTHIUREA DERIVATIVES.** Two of the fifteen acids studied (H and R acids) do not yield insoluble benzoyl derivatives but are readily characterized by means of benzylisothiurea. (At the outset of this work attempts to make general use of this reagent for characterizing all the acids failed in the majority of cases.)

The reagent is prepared by the method used by Chambers and Scherer (4) by adding, with stirring, 126.5 grams of benzyl chloride to a solution of 76 grams of thiourea in 200 ml. of 40 per cent alcohol and warming 15 minutes on the steam bath. On cooling, the benzylisothiurea separates and is recrystallized several times from 40 per cent alcohol (m. p. 176° C.).

The derivatives are prepared by dissolving 0.1 gram of the sulfonic acid, or its sodium salt, and 0.2 gram of benzylisothiurea separately in 5-ml. portions of approximately 0.2 N hydrochloric acid. Both solutions are heated to boiling and mixed. Upon cooling rapidly the derivative separates as a white crystalline precipitate. It is filtered, recrystallized once from 6 ml. of hot 0.2 N hydrochloric acid, and dried.

For microscopic examination the derivative is crystallized from a hot 1 per cent solution in 0.2 N hydrochloric acid by cooling until crystal nuclei just form, then allowing to stand at room temperature until a moderate amount of crystals has formed.

The properties and description of the acids studied and their derivatives are given in Table I. The purification procedure is that applied to the acid or its sodium salt (which-

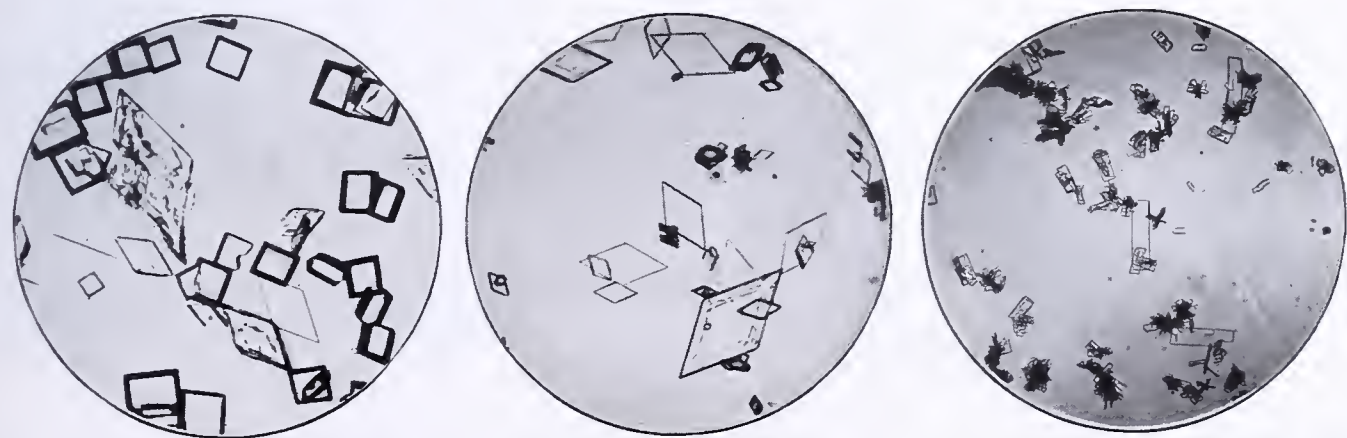


FIGURE 2. 1-NAPHTHYLAMINE-6-SULFONIC ACID (CLEVE'S ACID 1,6)  
Left. Free acid from hot solution      Center. Free acid from cold solution      Right. Benzoyl derivative



TABLE I. PROPERTIES OF NAPHTHALENE-

Substance	Purification procedure	Physical appearance	Free Acids or Sodium Salts	
			Hot solution	Microscopic Appearance Cold solution
1 - Naphthylamine - 7 - sulfonic acid (Cleve's acid 1,7)	Usual	Pure acid, flesh-colored with slight lavender cast	Almost square rectangular plates from concentrated solution	Irregular plates not as large or square as from hot; also dendritic clusters
1 - Naphthylamine - 6 - sulfonic acid (Cleve's acid 1,6)	Usual	Pure acid, light flesh color	From concentrated solution first mass of narrow rectangular needles rapidly changing to square crystals with occasional diamond	From dilute solution diamonds almost exclusively
1 - Naphthylamine - 5 - sulfonic acid (Laurent's acid)	Solution in sodium carbonate on standing overnight deposits dark material which is filtered off before precipitating free acid	Pure acid, pink	.....	Clusters and rosettes of long narrow rods from dilute solution. If solution is too concentrated, crystals very small
2 - Naphthylamine - 6 - sulfonic acid (Brönner's acid)	Usual	Pure acid, light flesh color	Elongated eight-sided plates and octahedra from concentrated solution. Considerable clustering and multiple twinning	Indefinite
2 - Naphthylamine - 1 - sulfonic acid (Tobias acid)	Usual	Pure acid, pink color	.....	Long prisms, much multiple twinning from dilute solution. By adding excess of free acid to sodium carbonate solution, filtering, and acidifying slightly with dilute hydrochloric acid, diamond shaped plates form. Occasional hexagonal plate
1 - Naphthylamine - 4 - sulfonic acid (naphthionic acid)	Usual	Pure acid, very light flesh color	Indefinite	Dendrites with occasional spherulite of rectangular needles
2 - Naphthol - 6 - sulfonic acid (Schaeffer's acid)	Dissolving sodium salt in least amount of hot water, treating with Darco and filtering hot. On cooling considerable salt crystallizes. Complete precipitation obtained by adding sodium chloride. Recrystallized similarly	Pure sodium salt is white	.....	Adding excess of sodium salt to cold water, gently warming to dissolve, cooling under tap until crystal nuclei appear, allowing to stand at room temperature, dense spherulites of needles form with occasional radiating narrow rectangular plates
1 - Naphthol - 4 - sulfonic acid (Neville and Winther's acid)	Strong aqueous solution treated with Darco and filtered. Filtrate acidified with hydrochloric acid and evaporated to dryness on steam bath. Residue extracted with 90% alcohol and alcohol evaporated	Purified acid is light gray color	.....	Precipitating from very concentrated solution with solid sodium chloride, tiny, almost circular flowerlike particles form which exhibit no apparent crystal-line structure
1,8 - Aminonaphthol - 4 - sulfonic acid (S acid)	Usual	Pure acid, light gray	.....	From dilute solution long slender needles inclined to cluster in dendritic forms
2,5 - Aminonaphthol - 7 - sulfonic acid (J acid)	Usual	Pure acid, flesh-colored	Diamond - shaped crystals from dilute solution; also a few dendritic clusters of long rectangular rods	Featherlike crystals from dilute solution
2,8 - Aminonaphthol - 6 - sulfonic acid (Gamma acid)	Usual	Pure acid, light gray, almost white	Dendrite of long narrow needles from dilute solution by cooling under tap until crystal nuclei appear, then allowing to stand at room temperature. Occasionally an indefinite rosette is also seen	.....
2 - Naphthylamine - 6,8 - disulfonic acid (amino G acid)	Acid dissolved in least amount of warm water. After cooling, precipitated by adding absolute alcohol and reprecipitated similarly	Pure acid is light cream color	.....	From concentrated solution masses of short fine needles considerably clustered
2 - Naphthol - 3,6 - disulfonic acid (R acid)	Sodium salt digested with cold 80% alcohol and alcohol discarded. Salt dissolved in small amount of water, treated with Darco, filtered, and precipitated by adding 95% alcohol	Pure sodium salt is light cream color	Rapidly cooling, saturated aqueous solution of sodium salt, short fine needles formed	.....
2 - Naphthol - 6,8 - disulfonic acid (G acid)	Sodium salt dissolved in least amount of hot water, alcohol added to about 80% strength and solution treated with Darco and filtered. Sodium salt precipitated by adding ether to filtrate and reprecipitated similarly	Pure sodium salt is white	Adding excess of sodium salt to cold water, warming to dissolve and cooling rapidly, glistening elongated rectangular prisms formed	.....
1,8 - Aminonaphthol - 3,6 - disulfonic acid (H acid)	Acid sodium salt dissolved in hot water, treated with Darco, filtered, and precipitated from filtrate by adding alcohol. Reprecipitated similarly	Pure acid sodium salt is pale green, almost white	Short narrow rectangular rods showing some dendrites and spherulites by rapidly cooling concentrated aqueous solution	.....



# SULFONIC ACIDS AND THEIR DERIVATIVES

During preparation	Characteristics of Benzoyl Derivatives		Optical Data on Derivatives				
	Microscopic appearance		Extinction	Sign of elongation	$n_a$	$n_o$	Figure
Soluble. Addition of moderate amount of salt gives light pink lustrous precipitate	Masses of shield-shaped plates clustered in beautiful rosettes		Parallel	Negative	1.685	1.606	1
Forms rapidly as pink floating precipitate. Not readily soluble in cold water	Rectangular plates, some fairly large. Smaller ones inclined to cluster in rosettes		Parallel	Positive	1.628	1.646	2
Soluble. Moderate amount of salt gives pink precipitate	When first formed consists of large oval plates considerably clustered, changing rapidly to large masses of piled-up plates with practically no individuals, but frequently showing parts of what appear to be elongated hexagons. Compensation not obtainable with certainty due to piling up and lack of individuals. Indices of refraction readily obtained on broken fragments		Parallel	..	1.633	1.576	3
Forms as flesh-colored precipitate, not readily soluble in cold water. Salts out easily	Dimorphous. (a) By usual salting out procedure dendrites of long bayonet-shaped crystals form (b) By cooling bot 1% aqueous solution until precipitation starts, then allowing to stand at room temperature, plates varying from square to elongated rectangles obtained. If crystallization has been rapid longer forms predominate Extinction poor and occasional isotropic crystal seen. Most views show one hrush of a biaxial interference figure. In several bours to a day crystals revert to form (a)		Parallel	Negative	Slightly under 1.71	1.612	4
Forms slowly as white precipitate, readily soluble in water but precipitated by small amount of salt	Fan-shaped clusters of long rods. At times spherulite of rods seen		Parallel	Negative	1.703	1.632	5
Forms very slowly as small amount of granular pink precipitate. Addition of considerable salt gives heavy precipitate	Masses of diamond or rhomb-shaped plates closely clustered. Individuals rare. In position of extinction crystal so aligned that direction through acute angles is parallel to cross hairs. Indices of refraction are given for crystals oriented in these positions. Slow component of crystal perpendicular to long direction. In clean-cut face observed crystal angles are apparently 76° and 104°		Ohlique 38°	..	1.653	1.537	6
Forms rapidly as granular white precipitate. Not readily soluble in water and precipitates with a small amount of salt	Fan-shaped fernlike clusters of tiny rectangular needles, best recrystallized from boiling 1% aqueous solution adding few drops of alcohol if necessary for solution, and allowing to cool at room temperature		Parallel	Positive	1.628	1.646	7
Forms instantly as gray gelatinous precipitate, moderately soluble in water, salts out readily	Precipitated in usual manner microcrystals of very little character obtained. Adding 20% sodium chloride solution dropwise to cold 0.25% aqueous solution of derivative until slight cloud forms, same microcrystals obtained; if allowed to stand overnight with test tube uncorked, upon shaking vigorously glistening rhomb-shaped plates form. Rhombs difficult to obtain as precipitation conditions are critical. Dilute solution, very little sodium chloride, prolonged standing, and violent agitation assist in formation. Extinction given when long edge of rhomb aligned with cross hair. In clean-cut crystal face observed crystal angles are apparently 70.5° and 109.5°. Refractive indices taken in mixture of methylene iodide and carbon tetrachloride. Slow component of crystal makes 30.6° angle with long direction of crystal		Ohlique 30.6°	..	1.654	1.460	8
Solution rapidly turns yellow and derivative forms as grayish gelatinous precipitate, readily soluble in water but precipitates with small amount of salt	Large fuzzy flowerlike spherulites with little crystalline character when first precipitated. On standing a day or so moderately large needles form, suitable for obtaining optical data. If grown slowly by adding 20% sodium chloride solution dropwise to cold 0.25% aqueous of derivative until faintly cloudy, upon keeping overnight with test tube uncorked, very dense spherulites of needles with thick radiating prisms obtained		Parallel	Negative	1.684	1.662	9
Soluble. Salted out rapidly is gummy, but if salt added to incipient precipitation and allowed to stand half hour crystalline precipitate obtained	Dense spherulites and dendrites of long flexihle needles distorted into curved forms by cover glass. If crystallized more slowly by adding one drop of 20% sodium chloride solution to 2 ml. of 1% cold aqueous solution of derivative, same form obtained but needles stronger		Parallel	Positive	1.629	1.696	10
Benzoylation occurs rapidly and liquid foams like soap solution. Derivative only partially precipitates but small quantity of salt gives pink, lustrous, gummy precipitate, readily soluble in water. Even when precipitated slowly gummy product obtained which crystallizes on standing overnight	Salt must be added very slowly to precipitate only trace of crystal nuclei. Upon standing several hours it appears as black dots, extremely dense spherulites of microneedles. Individuals from broken masses, although small, suitable for obtaining optical data. If crystallized too rapidly a useless gummy mass results		Parallel	Negative	Over 1.71	1.624	11
Soluble. Separates as bulky white precipitate upon adding considerable salt	Extremely long flexihle needles clustered to resemble tufts of hair		Parallel	Negative	1.691	1.510	12
Benzoyl derivative very soluble and cannot be satisfactorily salted out. Benzylisothiurea readily forms insoluble derivative and is used for characterizing acid	Crystallized from 1% solution rosettes of plates form. From more dilute solution (0.5%) long rectangular rods, many closely clustered in spherulites. By progressively diluting and examining 1% solution, both forms (plates and rods) may be obtained together		(Plates) Parallel Positive (Rods) Parallel Positive	Positive	1.591 1.552	1.617 1.697	13
Soluble. Separates as bulky white precipitate upon adding considerable salt	Extremely long rods resembling derivative of 2-naphthylamine-1-sulfonic acid but longer and less clustered		Parallel	Negative	1.681	1.547	14
Benzoyl compound very soluble and cannot be salted out. Benzylisothiurea readily forms insoluble derivative and is used for characterizing this acid	Crystallized from 1% solution dense spherulites of long narrow needles. Fast component of crystal makes 17° angle with long direction		Ohlique 17°	..	1.592	1.694	15



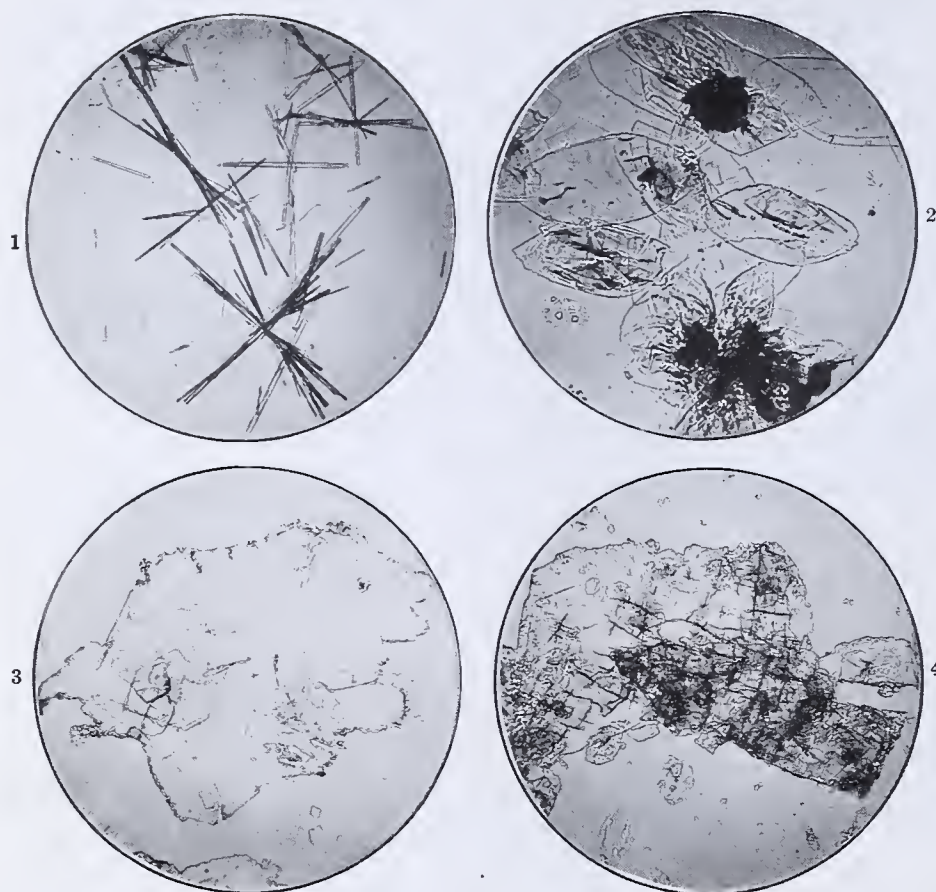


FIGURE 3. 1-NAPHTHYLAMINE-5-SULFONIC ACID (LAURENT'S ACID)

- |   |                                      |
|---|--------------------------------------|
| 1. Free acid from cold solution             | 3. Benzoyl derivative after standing |
| 2. Benzoyl derivative as first precipitated | 4. Benzoyl derivative, another view  |

ever is the more usually met with or easily handled) before preparing the derivative. The designation "usual" refers to precipitation from sodium carbonate solution with hydrochloric acid, referred to above. The physical appearance of the pure acid or salt is stated in the third column. Unless otherwise noted, the free acids were precipitated with dilute hydrochloric acid (1 to 3 of water) from their solution in sodium carbonate.

The microscopic appearance of the benzoyl derivatives is described, after recrystallization by the standard procedure outlined, or as stated in the table.

In the section under Optical Data on Derivatives indices of refraction are taken in the two positions of extinction and are noted as  $n_a$  and  $n_o$ . When the long direction of the crystal is aligned with the 6 to 12 o'clock cross hair, the refractive index has been designated as  $n_o$  (ordinate); when aligned with the other cross hair, as  $n_a$  (abscissa). For crystals showing oblique extinction, the first position ( $15^\circ$ ) is  $n_o$ , and the next ( $105^\circ$ ) is  $n_a$ .

These refractive indices do not necessarily correspond to  $\omega$  and  $\epsilon$  or  $\alpha$ ,  $\beta$ , or  $\gamma$  but are more readily obtained. They are taken in mixtures of methylene iodide and xylene with white light at  $20^\circ \text{C}$ .

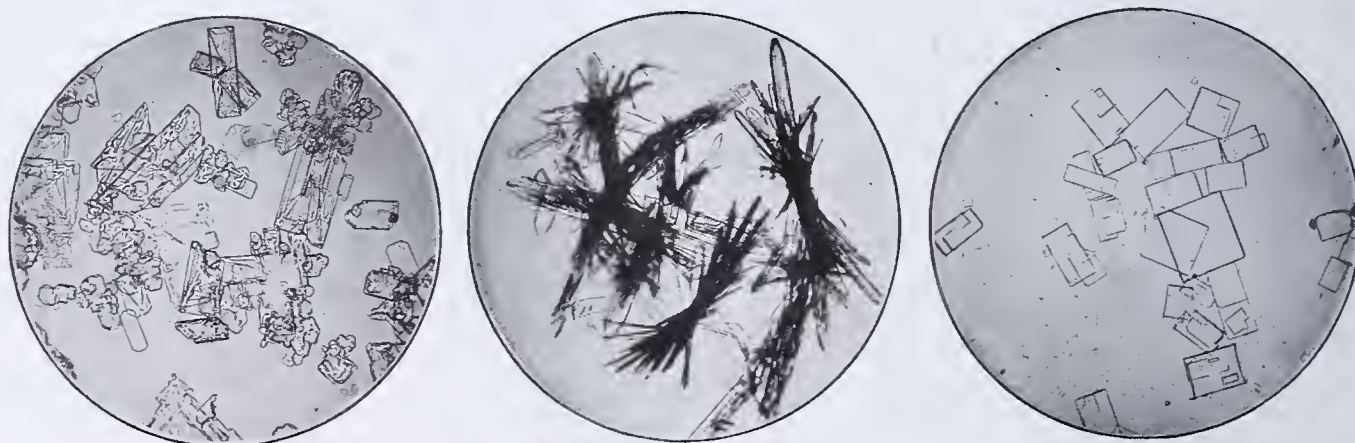


FIGURE 4. 2-NAPHTHYLAMINE-6-SULFONIC ACID (BRÖNNER'S ACID)

- |      |                             |         |  |
|------|-----------------------------|---------|--|
| Left | Free acid from hot solution | Center. | Benzoyl derivative crystallized from salt solution |
|      |                             | Right.  | Benzoyl derivative crystallized from water         |

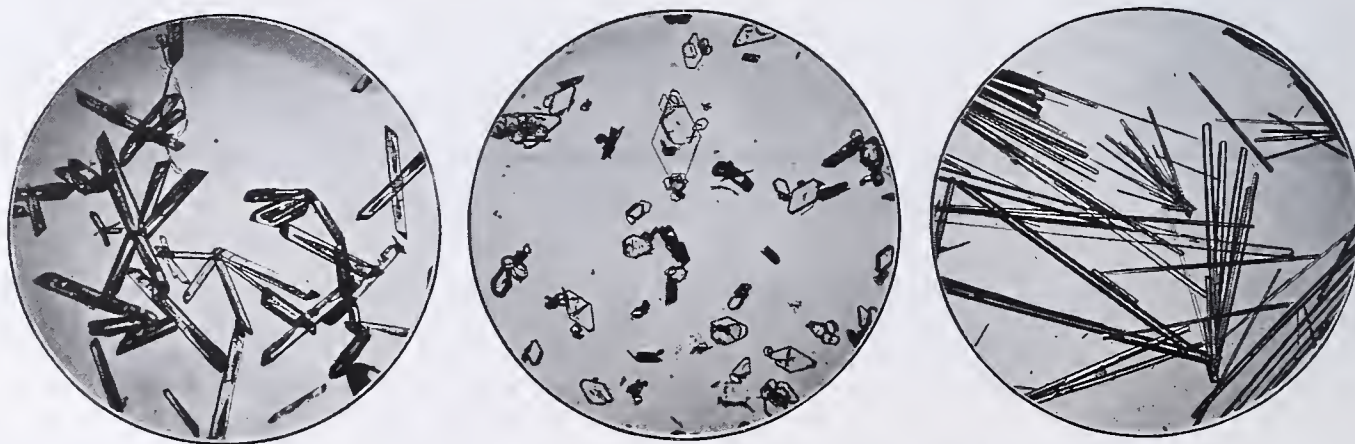


FIGURE 5. 2-NAPHTHYLAMINE-1-SULFONIC ACID (TOBIAS ACID)

- |      |                                   |         |   |
|------|-----------------------------------|---------|---|
| Left | Free acid from cold acid solution | Center. | Free acid from cold almost neutral solution |
|      |                                   | Right.  | Benzoyl derivative                          |



In general, interference figures are not readily observable in the orientations visible.

### Separations by Means of Benzoyl Derivatives

The varying solubilities of the derivatives suggested the possibility of separating various acids by this means. Table II summarizes the solubilities of the benzoyl compounds studied.

A trial separation based upon the solubilities shown in Table II was made by benzoylating a mixture of 0.2 gram each of 1-naphthylamine-7-sulfonic acid and 2-naphthol-6-sodium sulfonate in the usual manner, using proportional amounts of reagents.

**PRECIPITATE.** The precipitate was filtered by suction, washed with a little cold water, dissolved in 20 ml. of warm water, cooled, precipitated with the least possible amount of salt, and reprecipitated similarly a second time. When recrystallized for microscopic examination in the usual manner it showed the characteristic fan-shaped clusters of the benzoyl derivative of Schaeffer's acid (Figure 7, 2).

**FILTRATE.** Salt was added until a slight precipitate formed which was filtered off and discarded (to remove any residual derivative of Schaeffer's acid). The bulk of the derivative was then salted out and recrystallized as usual until neutral. When recrystallized for microscopic examination shield-shaped rosettes

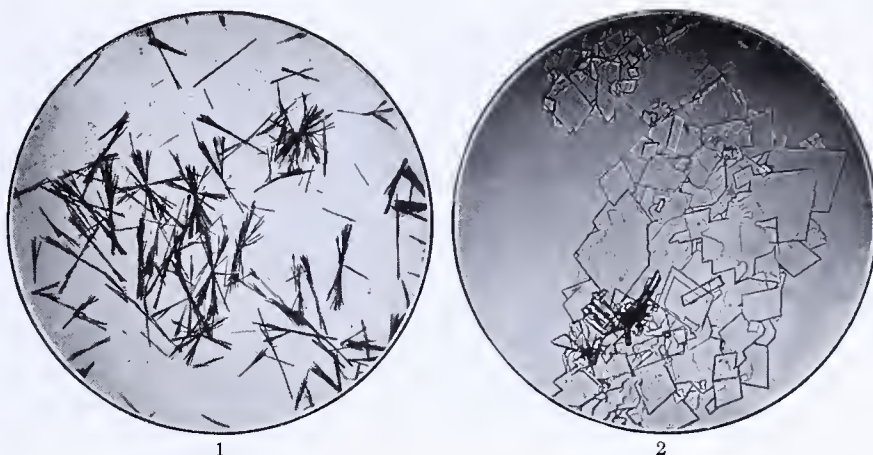


FIGURE 6. 1-NAPHTHYLAMINE-4-SULFONIC ACID (NAPHTHIONIC ACID)  
1. Free acid from cold solution 2. Benzoyl derivative

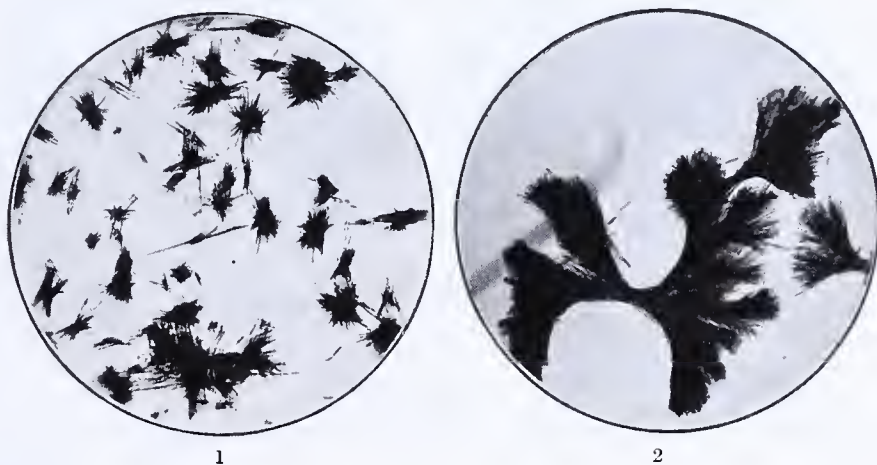


FIGURE 7. 2-NAPHTHOL-6-SULFONIC ACID (SCHAEFFER'S ACID)  
1. Sodium salt from cold saturated solution 2. Benzoyl derivative

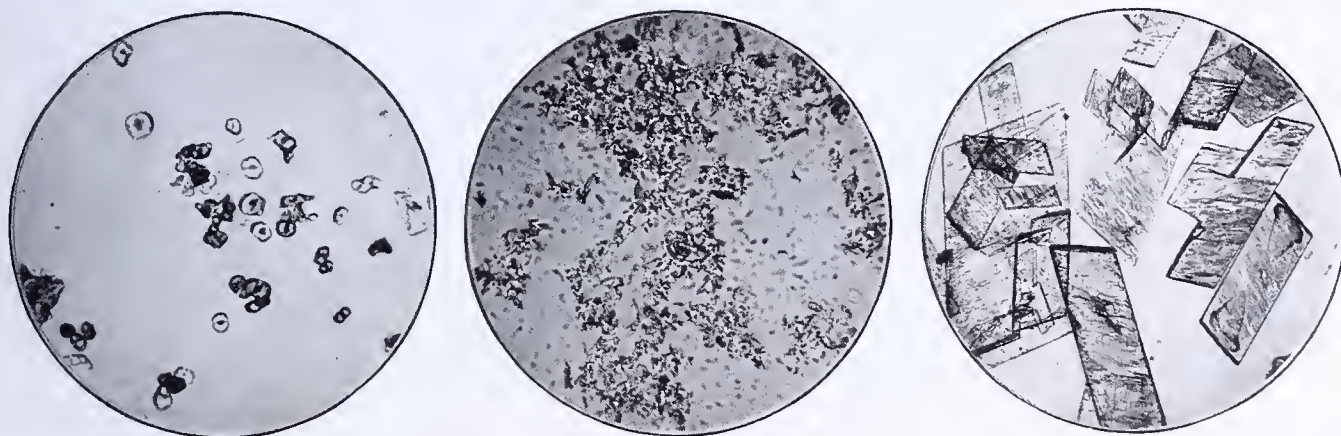


FIGURE 8. 1-NAPHTHOL-4-SULFONIC ACID (NEVILE AND WINTHER'S ACID)  
Left. Free acid salted out from cold concentrated solution Center. Benzoyl derivative as first precipitated  
Right. Benzoyl derivative after standing

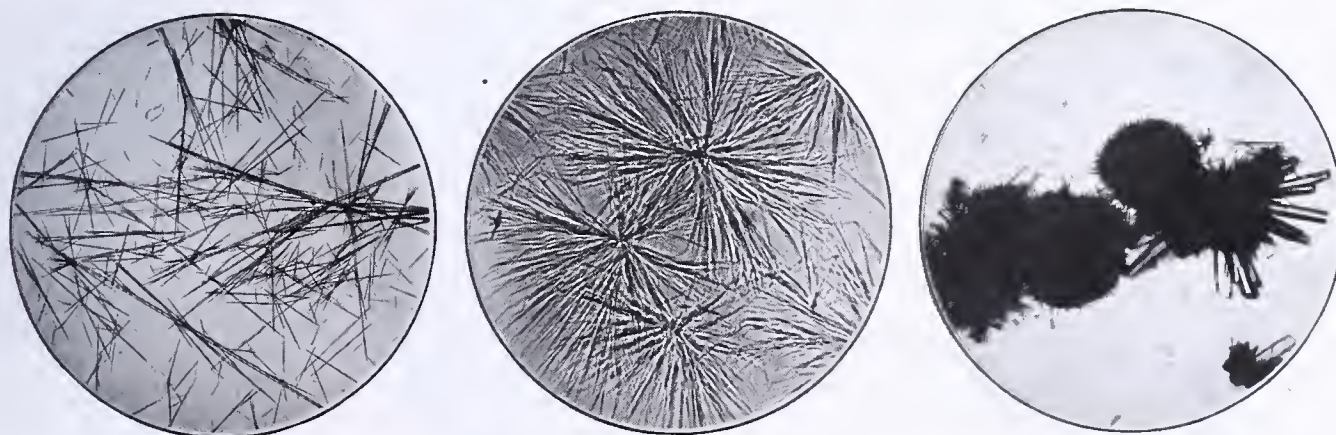


FIGURE 9. 1,8-AMINONAPHTHOL-4-SULFONIC ACID (S ACID)  
Left. Free acid from cold solution Center. Dibenzoyl derivative, ordinary precipitation  
Right. Dibenzoyl derivative grown slowly from dilute solution



of the benzoyl derivative of Cleve's acid 1,7 were obtained (Figure 1, right).

This result indicates that clean-cut separations are possible.

In this study no unusual types of compounds were prepared or new or unusual syntheses involved in the preparation of derivatives. In addition, many of the compounds which were made were isomeric and consequently it was felt that analyses of type compounds would be satisfactory and representative of groups.

Analyses were made of the following types: a monobenzoyl compound, a dibenzoyl compound, and a benzylisothiourea derivative. Nitrogen was determined by the Kjeldahl method and sulfur with the Parr bomb.

**MONOBENZOYL DERIVATIVE.** 2-Benzoylnaphthylamine-1-sodium sulfonate ( $C_{10}H_6SO_3Na.NH.CO.C_6H_5$ ).

Nitrogen calculated, 4.02 per cent; found, 3.89 per cent. Sulfur calculated, 9.17 per cent; found, 8.99 per cent.

**DIBENZOYL DERIVATIVE.** 2,5-Dibenzoylaminonaphthol-7-sodium sulfonate [ $C_{10}H_5SO_3Na.NH.O.(CO.C_6H_5)_2$ ].

Nitrogen calculated, 2.98 per cent; found, 3.08 per cent. Sulfur calculated, 6.8 per cent; found, 6.63 per cent.

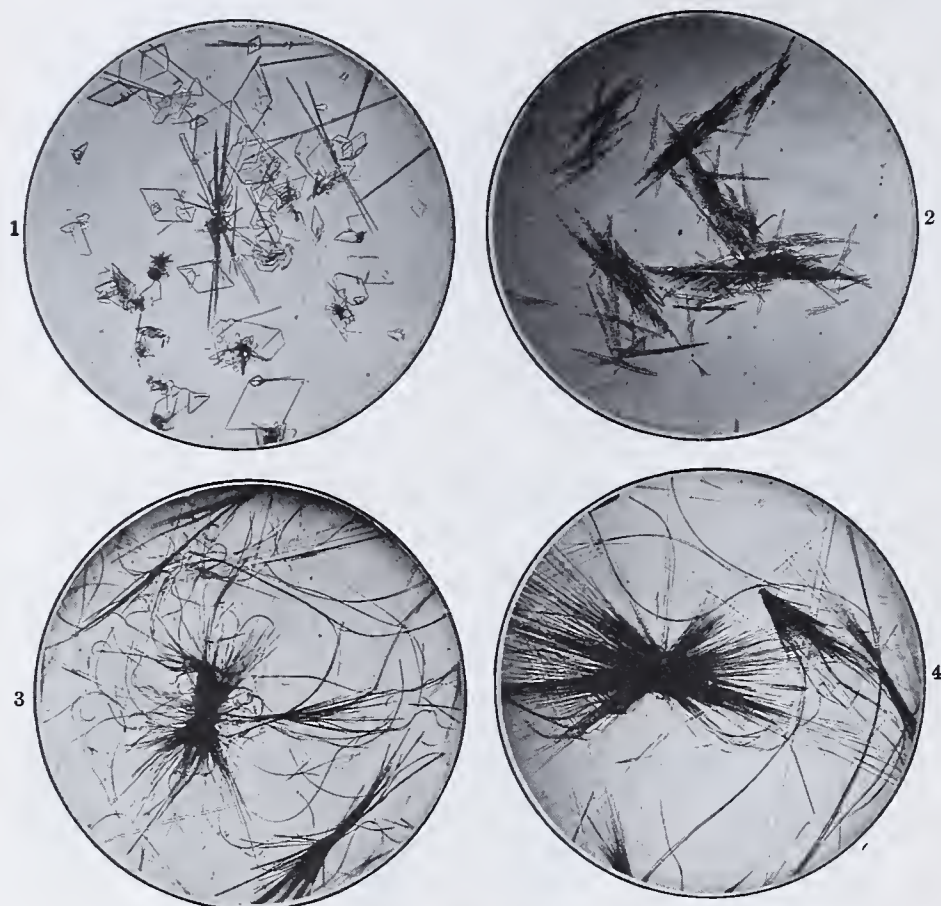


FIGURE 10. 2,5-AMINONAPHTHOL-7-SULFONIC ACID (J ACID)

- |  |  |
|--|--|
| 1. Free acid from hot dilute solution  | 3. Dibenzoyl derivative                          |
| 2. Free acid from cold dilute solution | 4. Dibenzoyl derivative precipitated more slowly |

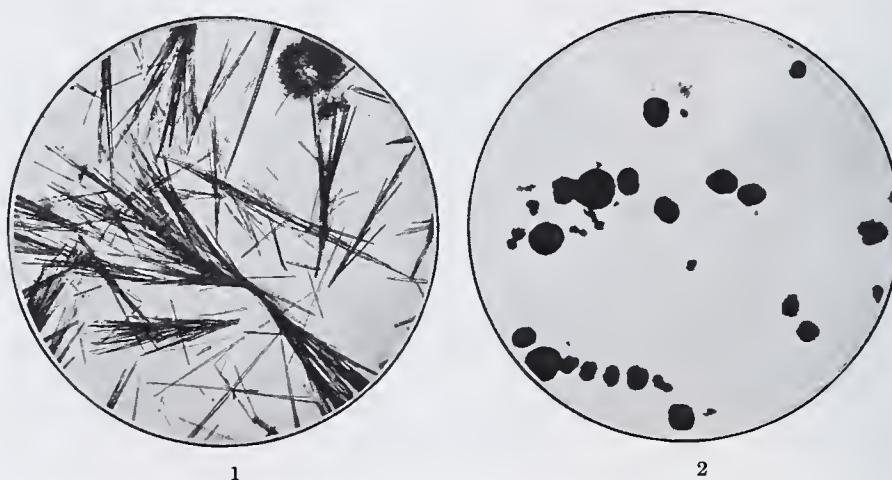
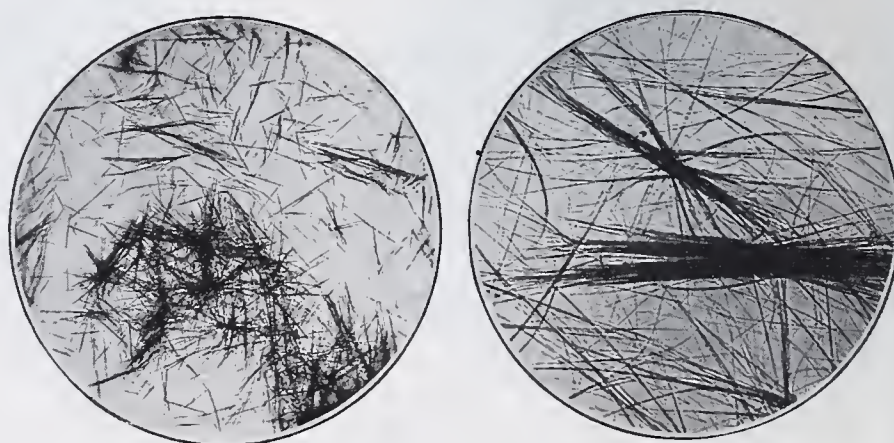


FIGURE 11. 2,8-AMINONAPHTHOL-6-SULFONIC ACID (GAMMA ACID)

- |                                      |
|--------------------------------------|
| 1. Free acid by cooling hot solution |
| 2. Dibenzoyl derivative              |

FIGURE 12 (Right). 2-NAPHTHYLAMINE-6,8-DI-SULFONIC ACID (AMINO G ACID)

- |                                 |
|---------------------------------|
| 1. Free acid from cold solution |
| 2. Benzoyl derivative           |





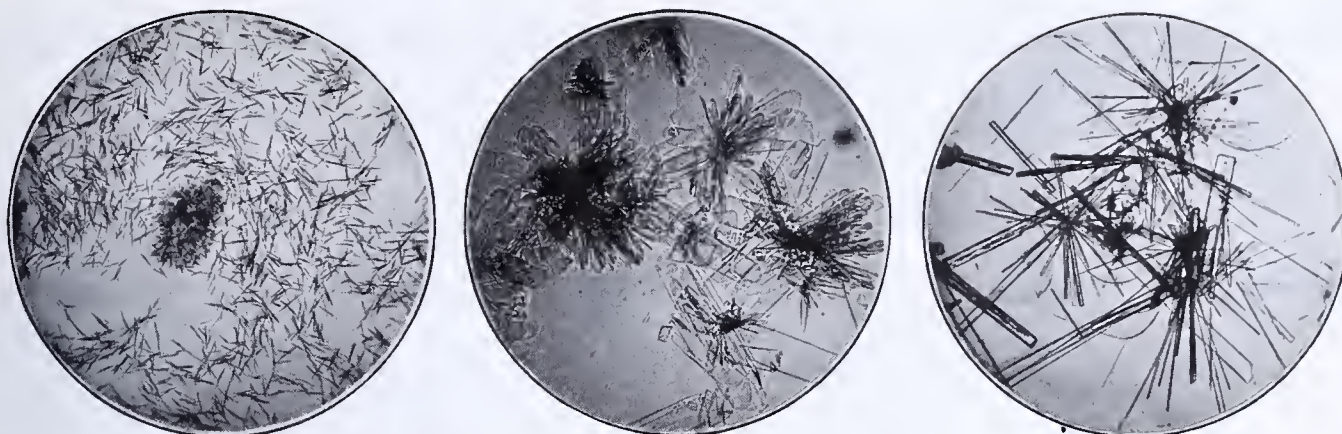


FIGURE 13. 2-NAPHTHOL-3,6-DISULFONIC ACID (R ACID)

Left. Sodium salt from hot concentrated aqueous solution  
Center. Benzylisothiurea derivative from 1 per cent solution  
Right. Benzylisothiurea derivative from 0.5 per cent solution

BENZYLISOTHIUREA DERIVATIVE OF 2-NAPHTHOL-3,6-DISULFONIC ACID  $[C_{10}H_6.OH(SO_3H.NH_2.NH:CS.CH_2.C_6H_5)_2]$ .  
Nitrogen calculated, 8.81 per cent; found, 8.70 per cent.  
Sulfur calculated, 20.00 per cent; found, 20.12 per cent.

### Summary and Conclusions

A rapid and relatively simple method has been developed for the microscopic identification of a number of important naphthylamine, naphthol, and aminonaphthol sulfonic acids by means of their benzoyl derivatives.

TABLE II. SOLUBILITIES OF BENZOYL DERIVATIVES

Acids Precipitated during Benzoylation	Acids Not Precipitated during Benzoylation
2-Naphthylamine-1-sulfonic acid (Tobias acid), readily soluble in water, salts out easily	1-Naphthylamine-7-sulfonic acid (Cleve's acid 1,7), precipitates with a moderate amount of salt
1-Naphthylamine-6-sulfonic acid (Cleve's acid 1,6), not readily soluble in water	1-Naphthylamine-5-sulfonic acid (Laurent's acid), precipitates with a moderate amount of salt
2-Naphthylamine-6-sulfonic acid (Brönner's acid), difficultly soluble in cold water	2,5-Aminonaphthol-7-sulfonic acid (J acid), precipitates with a moderate amount of salt
1-Naphthol-4-sulfonic acid (Neville and Winther's acid), moderately soluble in water, salts out readily	2,8-Aminonaphthol-6-sulfonic acid (Gamma acid), gummy precipitate with a moderate amount of salt
2-Naphthol-6-sulfonic acid (Schaeffer's acid), very difficultly soluble in cold water, not very soluble in hot	2-Naphthol-6,8-disulfonic acid (G acid), requires a large amount of salt for complete precipitation
1,8-Aminonaphthol-4-sulfonic acid (S acid), readily soluble in water, precipitates with a small amount of salt	2-Naphthol-3,6-disulfonic acid (R acid), only a small amount of precipitate with saturated salt
	1,8-Aminonaphthol-3,6-disulfonic acid (H acid), cannot be salted out

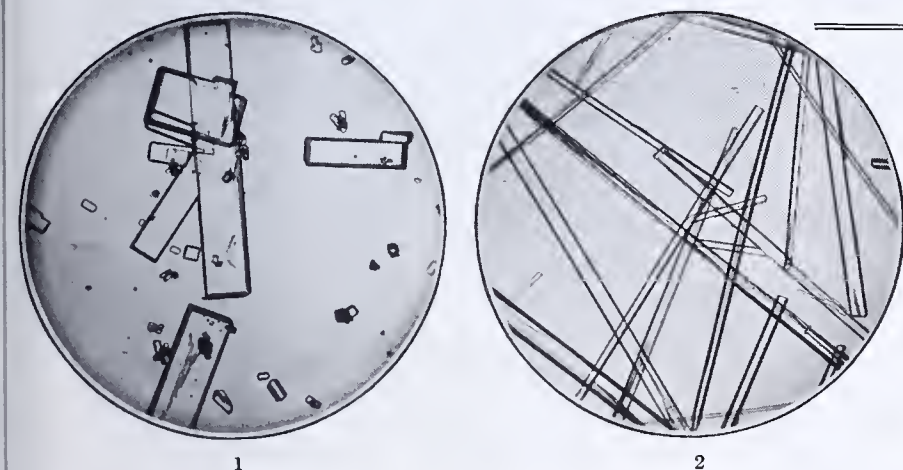


FIGURE 14. 2-NAPHTHOL-6,8-DISULFONIC ACID (G ACID)

1. Sodium salt from saturated aqueous solution      2. Benzoyl derivative

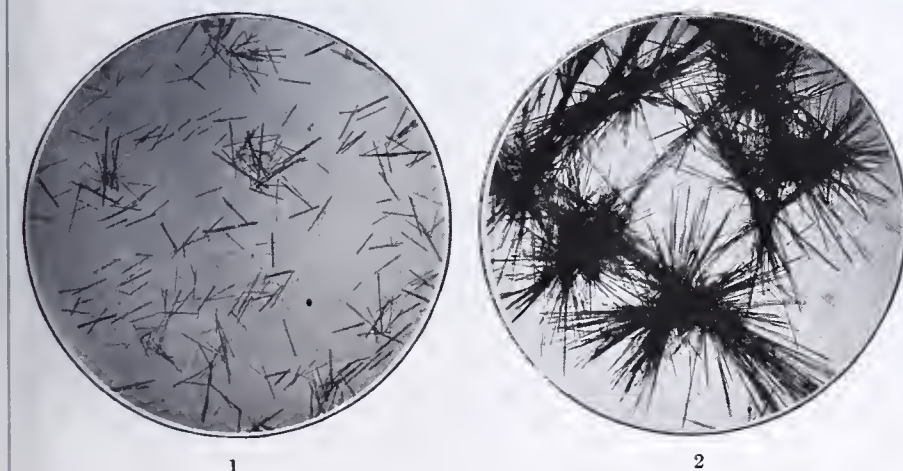


FIGURE 15. 1,8-AMINONAPHTHOL-3,6-DISULFONIC ACID (H ACID)

1. Acid sodium salt from hot water      2. Benzylisothiurea derivative

The procedure has been standardized so as to be applicable to the entire group of acids; only small amounts of material are required.

The benzoyl derivatives offer a possible method of separation of some of the acids.

The characteristics and microscopic appearance of fifteen of these sulfonic acids and their derivatives have been tabulated, including optical data for the latter, and photomicrographs of characteristic forms have been prepared.

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# Angular Constants of Microcrystalline Profiles and Silhouettes in the Conclusive Identification of Substances

## Octagons of a Cinchophen Hydrochloride Hydrate and of Silver Dichromate

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REVERSING the earlier method (2), this paper deals with the least symmetrical of the flat tabular crystals encountered in the two-dimensional crystallography of plane geometry.

Whether symmetrical or asymmetrical, the octagon is ordinarily the most complex geometrical form produced by the methods previously outlined (2). The directions of its eight sides fix positively the angles and patterns of all simpler platy crystals, which may be considered as derived from the octagon by the prolongation of certain of its sides in the plane established by its boundaries. Thus, by establishing the values of four angles in sequence, or, in the totally asymmetric case, eight, on the octagon, constants will be available for calculating most of the angles and forms to be found on flat crystals encountered in microchemical practice.

This objective is accomplished by measuring all the angles, in order, on selected perfect octagonal crystals. If of low symmetry, four angles in sequence will be different, as will be eight in total asymmetry. Clockwise or counterclockwise distinctions are ignored. The values of identical angles are then tabulated one under the other and averaged, and conclusions are drawn as to the magnitude of the component angles and their sequence. The sequences thus established can then be recognized on forms other than the octagon and incorporated to reinforce the data already collected. The

same values can be identified on forms where there is no sequence, as in the parallelogram or asymmetric quadrilateral which incorporates every fifth angle of the octagon. Lastly, those angles not occurring on the octagon are measured and tested for compatibility with those already established. For example, an asymmetric quadrilateral of silver dichromate that approaches a rectangle is found. Its angles do not occur on the octagonal crystal of the same substance, but will be found, by measurement, to be the same as those calculated by simple plane geometry for the figure resulting by prolonging alternate sides of the octagon, the angles and sequence of which have been previously established. Compatibility of angles, thus interpreted, is as diagnostic as their identity.

In evaluating angular data for the establishment of corresponding constants, it is soon realized that they vary in precision because certain angles are better developed both in size and perfection than are others. Those with long sides and large angular magnitude can often be established within  $\pm 0.2^\circ$  or even better (1). Also, the size and perfection of the angle often depend upon the geometrical shape of the crystal on which it occurs, so that the value determined under more favorable conditions may advantageously be transferred to the position elsewhere established.

Data tending to support this thesis are presented for a cinchophen (2-phenylquinoline-4-carboxylic acid) hydrochloride hydrate from four different sources and for silver dichromate.

### Preparation

Approximately 0.5 mg. of 2-phenylquinoline-4-carboxylic acid was dissolved in 0.5 ml. of concentrated hydrochloric acid at a boiling temperature and then allowed to cool spontaneously to room temperature. Violent agitation during or after cooling is necessary to bring down suitable crystals. If hairy trichites form, the solution is gently heated until they just dissolve, and the cooling and agitation are repeated. If the crystals are too well developed, the same procedure is followed, or solution, crystals, and all are poured upon a microscope slide and suitable shapes are allowed to develop by evaporation and cooling of the still warm solution. After the desired platy crystals are observed, the mother liquor is carefully poured off at a low pouring angle, and that remaining is gently blotted away by means of filter paper. Measurements are then made, as elsewhere directed (2), as soon as possible, since the crystals are stable for but a few hours at ordinary temperatures and humidity. The coarse seed crystals induce suitable large platy crystals, especially if the concentrated hydrochloric acid be diluted slightly with water (see Table I for the angular constants).

Silver dichromate crystals were deposited by spontaneously cooling a violently agitated nitric acid solution (1 to 1) of the salt produced by the interaction of the silver ion with excess chromic acid from reagent chromium trioxide, which was employed because of its solubility in strong alcohol. On subsidence of the silver dichromate after pouring the reaction mixture upon a microscope slide, the mother liquor was drained off and the residual crystals were washed free of reagent with

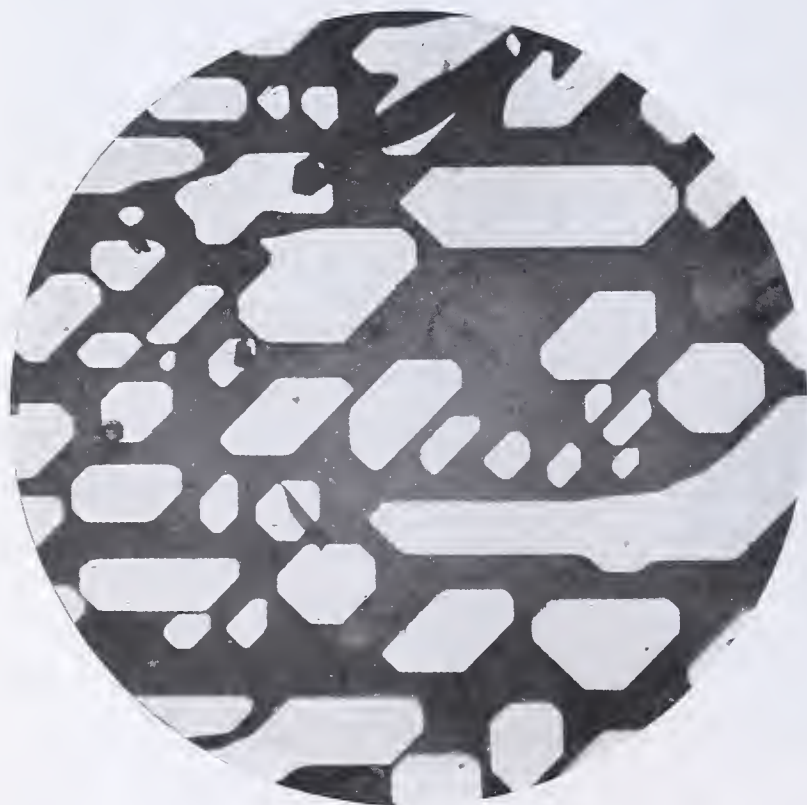


FIGURE 1. ETCH FIGURES ON A SINGLE CRYSTAL OF SILVER DICHROMATE



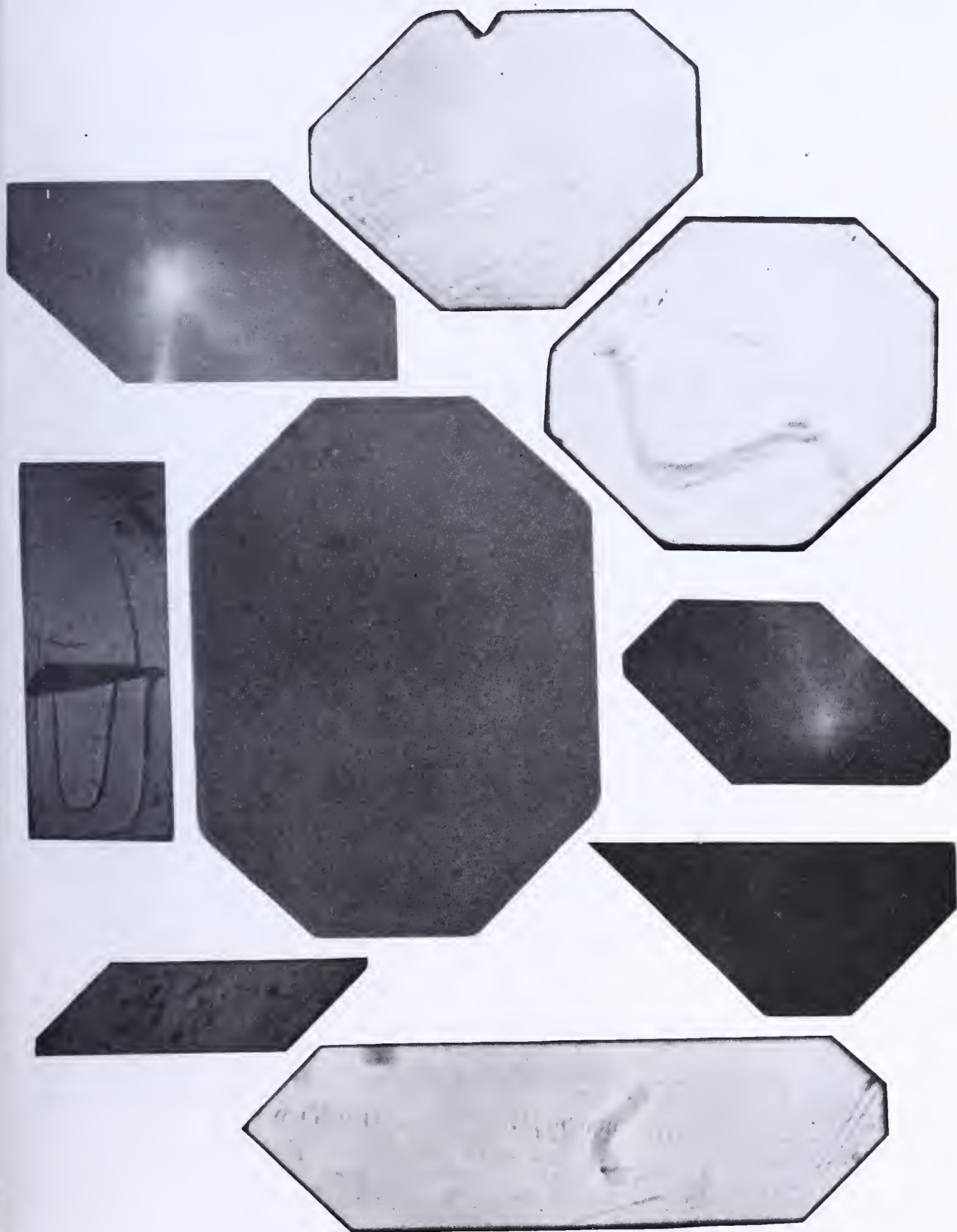


FIGURE 2. SILVER DICHROMATE CRYSTALS



strong alcohol. If desired, the crystals may be washed in the tube wherein they were originally precipitated, by decantation before transference to the slide for examination. The crystals are then measured as previously described (2) and the data recorded.

Checking Data from Unknown Substances

In general, checking against angular constants is the same as checking against any other constant such as melting point, boiling point, etc. However, in the completely asymmetric case, where a sequence of eight angular values on the octagon constitutes the constant and where compatibility as well as identity of angular magnitude is a factor, some explanation of method may be necessary. Obviously, if eight angles of an unknown substance have the same values and order as those of a known substance, the two are almost conclusively proved to be identical. Partial sequences from which the whole can be constructed likewise constitute valid direct proof. Pairs of opposite angles on quadrilaterals of the unknown, having identical values with the two fifth angles of the known octagon, are diagnostic, especially if the four different "parallelogramoids" theoretically possible can be found. Even a sufficient number of values for isolated single angles (ideally eight different ones) on the unknown would be satisfactory, aside from sequence, if identical with the octagon constants of the known substance.

Probably the simplest test for compatibility of angular values as contrasted with identity is found on quadrilaterals having no angles common with those on the octagon constant but easily derived therefrom by simple projection.

From its angular values, the fundamental octagon is accurately laid out on a drafting board, if the derived values are to be obtained by protractor measurement; if they are to be calculated, the octagon may be sketched and its angular values properly assigned. Next, a new angle is constructed by prolonging the appropriate sides of two adjacent angles of the octagon, which diminishes the angles and sides of the octagon by one to produce the heptagon. The new angle can be measured by a protractor or calculated from the plane geometry of poly-

gons. Systematic continuation of this process produces the desired quadrilateral with its derived constants, which may be compared with corresponding values directly observed on like geometrical forms found on crystals of the unknown substance.

Another instance of angular constants derived from the fundamental constants found upon the basic octagon may be cited.

Parallelogramlike quadrilaterals of "diamond" shape may be generated by prolonging the sides of the fifth angles, counting first and last, of the octagon.

Two of the angles of the figure thus formed are identical with the corresponding fifth angles of the octagon, while the two acute angles of the new figure are derived values or constants. These likewise can either be measured by protractor or calculated in a manner analogous to that described above by operating in two successive steps and employing the plane geometry of polygons.



FIGURE 3. CINCHOPHEN HYDROCHLORIDE

Obviously, almost any angle on practically any figure can be deduced by the procedure indicated.

Ordinarily, such complexities are not actually encountered and but little of the indicated method is required in a given case. Often the octagon is hard to find. Simpler forms are common; the octagon, a complex form, is seldom encountered because of its rarity. Many fields (microscopic) have to be searched before the octagon "key" form that enables the

TABLE I. DETERMINATION OF ANGLES AND SEQUENCE

Test	Maker	Angles								Related Angles		Sum
		A	B	C	D	E	F	G	H			
Octagon of Cinchophen Hydrochloride Hydrate												
I	E. K. 2913 <sup>a</sup>	129.30	142.90	141.95	126.10	129.80	140.90	142.80	126.50	..	..	1080.2
II	Mal. <sup>b</sup>	128.60	143.60	141.30	125.80	128.10	142.60	141.50	127.00	..	..	1078.5
III	Mal. <sup>b</sup>	128.85	144.20	141.30	126.40	128.70	143.80	140.90	125.90	..	..	1080.0
IV	E. K. 2913 <sup>a</sup>	128.30	142.30	142.40	125.70	128.80	143.00	141.50	126.80	..	..	1078.8
V	Unknown	128.40	143.10	142.00	126.00	128.60	143.25	141.85	126.25	..	..	1079.4
VI	Unknown	128.90	143.10	142.40	126.50	128.20	143.60	141.90	126.00	..	..	1080.6
VII	Mal. <sup>b</sup>	129.05	143.10	141.60	126.30	....	....	141.60	125.85	..	..	....
VIII	E. K. 2913 <sup>a</sup>	128.30	143.40	142.90	....	....	....	141.30	126.30	..	..	....
IX	Mal. <sup>b</sup>	129.60	142.60	140.90	....	....	....	....	127.10	..	..	....
X	E. K. 2913 <sup>a</sup>	128.40	143.40	142.60	....	....	....	....	....	..	..	....
XI	Unknown	128.70	....	....	....	128.60	....	....	....	..	..	....
XII	Unknown	128.90	....	....	....	128.35	....	....	....	..	..	....
XIII	Unknown	....	143.4	....	....	....	143.95	....	....	..	..	....
XIV	Mal. <sup>b</sup>	....	....	142.00	....	....	....	142.30	....	..	..	....
XV	Unknown	....	....	142.80	....	....	....	142.80	....	..	..	....
	Sum	1545.3	1575.1	1704.15	882.8	1029.15	860.2	1418.45	1137.70	..	..	....
	Av.	128.8	143.2	142.0	126.1	128.65	143.4	141.85	126.40	..	..	1080.4
Four different angles of octagon: 128.7, 143.3, 141.9, 126.25, constants												
Check (independent arrangement): 128.85, 143.05, 141.30, 126.3, constants												
Octagon of Silver Dichromate												
I	.....	136.5	134.8	133.8	134.8	136.1	134.6	133.7	135.1	..	..	1079.4
II	.....	136.4	134.9	133.7	135.0	136.0	134.3	133.7	135.6	..	..	1079.6
III	.....	136.6	134.6	133.8	135.2	136.0	134.9	133.9	134.6	..	..	1079.6
IV	.....	136.6	135.1	133.7	134.4	136.4	134.5	133.8	134.8	..	..	1079.3
V	.....	136.7	135.0	134.0	134.8	136.4	134.5	134.3	134.5	..	..	1080.2
VI	.....	136.3	134.9	...	...	135.5	135.2	133.7	134.1	88.8	..	898.5
VII	.....	...	...	...	...	136.1	134.5	134.0	...	91.2	43.5	539.3
VIII	.....	...	135.3	...	...	...	135.0	...	...	44.7	44.4	359.4
IX	.....	...	135.1	...	...	...	134.3	...	...	...	...	....
X	.....	...	135.2	...	...	...	134.7	...	...	45.3	45.0	360.2
XI	.....	...	135.3	...	...	...	134.7	...	...	45.2	44.7	359.9
XII	.....	...	134.9	...	...	...	134.0	...	...	45.4	45.4	359.7
XIII	.....	...	135.7	...	...	...	134.6	...	...	...	...	....
XIV	.....	...	135.4	...	...	...	134.7	...	...	45.0	44.7	359.8
XV	.....	...	135.3	...	...	...	134.6	...	...	45.1	44.9	359.9
XVI	.....	...	...	...	134.7	...	...	...	134.4	45.3	45.2	359.6
XVII	.....	...	...	134.4	...	...	...	133.8	...	46.5	45.0	359.7
	Av.	136.5	135.1	133.9	134.9	136.1	134.6	133.8	134.7	..	..	1079.6

<sup>a</sup> Eastman Kodak Co.      <sup>b</sup> Mallinckrodt Chemical Works.



simple forms to be explained, is found. This difficulty is encountered only in the research that establishes the constant.

### Illustrations

Figure 1 is an illustration of etch figures formed on a single crystal of silver dichromate by refluxing solvent flowing over a crystal plate lodged above the "water line." Parallelism of corresponding sides of identical angles on different forms is evident.

Figure 2 shows crystals of silver dichromate with the sides of identical angles parallel, as far as possible. Dark colors are crystals; light colors denote etch figures selected from Figure 1. On the octagons and heptagon the angle designated as *A* is at the top to the right and the others follow in

counterclockwise order. These figures are the principal ones from which angular data were taken.

Figure 3 is an octagon of cinchophen hydrochloride hydrate.

The last values of Table I constitute the constant to be recorded for the asymmetric octagon of silver dichromate. A quadrilateral of silver dichromate had the following angles: 88.9°, 91.7°, 88.2°, and 91.4°; sum, 360.2°.

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RECEIVED November 1, 1937. Presented before the Microchemical Section at the 95th Meeting of the American Chemical Society, Dallas, Texas, April 18 to 22, 1938. This is the second paper in a series; for the first, see reference (2).

## An Accurate Micromanometer

C. C. WINDING AND F. H. RHODES, Cornell University, Ithaca, N. Y.

THE differential micromanometer described below was designed and built to measure small pressure differentials with an accuracy at least equal to, if not greater than, the usual two-liquid manometers. Pressures larger than 2.5 cm. (1 inch) of water cannot be measured with this instrument, but this range is large enough for many of the differential pressures encountered in the flow of gases. It has been used satisfactorily for Pitot tube and pressure drop measurements in air ducts.

With the ordinary two-liquid micromanometers, the difficulty of locating the meniscus and parallax introduces unknown errors that may be as large as several hundredths of a millimeter. Since the level of the water in this manometer is measured by the completion of an electric circuit, and not by the visual location of a meniscus, these errors are not present. The absolute accuracy of the instrument depends chiefly on the accuracy of a micrometer screw which can easily be read to  $\pm 0.003$  mm. Because a slight amount of vibration is usually present, unless extreme precautions are observed in mounting the instrument, this accuracy cannot be attained in practice. This manometer has been in use for approximately one year, operated chiefly by students who had not even seen the instrument until just before taking readings. With this type of inexperienced operator, duplicate readings of a constant pressure usually do not deviate more than  $\pm 0.01$  mm.

from the average. In addition, a constant error due to the design of the instrument is present.

One end of the U-tube which forms the manometer is fixed in a pivot, while the other is free to rotate in a vertical plane. Thus the opposite end, where the measurements of levels are made, moves in an arc with the pivot at the center. The platinum wire which makes contact with the surface of the liquid in the manometer (Figure 1) remains at a fixed distance from the pivot, but the point of contact of the end of the micrometer screw and the plate that rests on it is free to move outward from the pivot as the angle of the manometer arm with the horizontal is increased. This outward movement must be permitted, as the arm carrying the contact plate is moving in a circle while the micrometer screw moves in a vertical line. A simple analysis of this construction reveals that the distance measured by the screw is not exactly the same as the vertical distance traveled by the end of the platinum wire in any deviation from the zero, or horizontal position. The difference between these two distances is the constant error of the instrument and is dependent on the angle of deviation from the zero position and the distance between the pivot and the point of the electrode in the opposite arm. The following derived relationship permits calculation of the magnitude of this deviation:

$$\Delta d = l(\tan \alpha - \sin \alpha)$$

where  $\Delta d$  is the error,  $l$  is the distance from the pivot to the platinum wire, and  $\alpha$  is the angle through which the instrument must be rotated in order to measure the difference in level caused by two different pressures. Although the error is directly dependent on the length of the manometer,  $l$ , the difference between the tangent and the sine decreases much more rapidly than the increase in  $l$ . When  $l$  is infinite this dif-

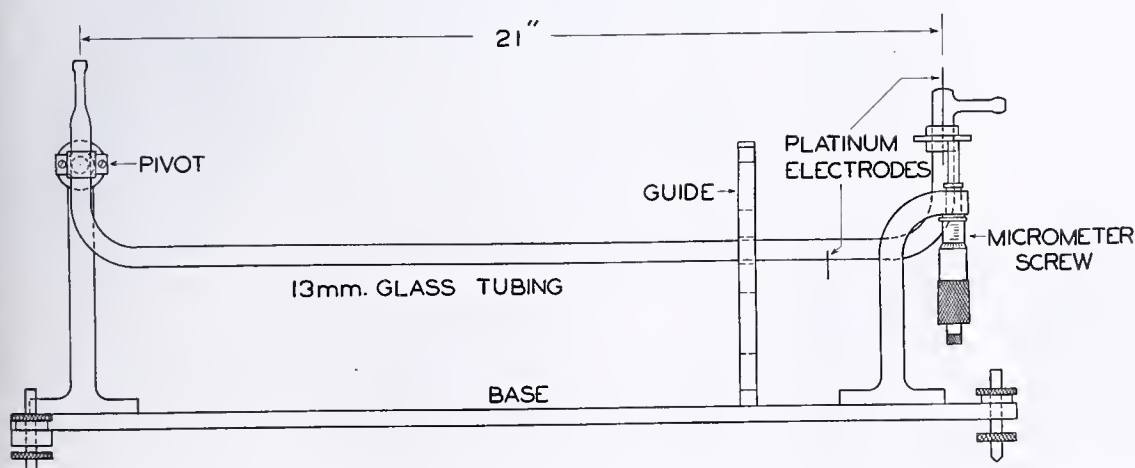


FIGURE 1. DIAGRAM OF MANOMETER CONSTRUCTION



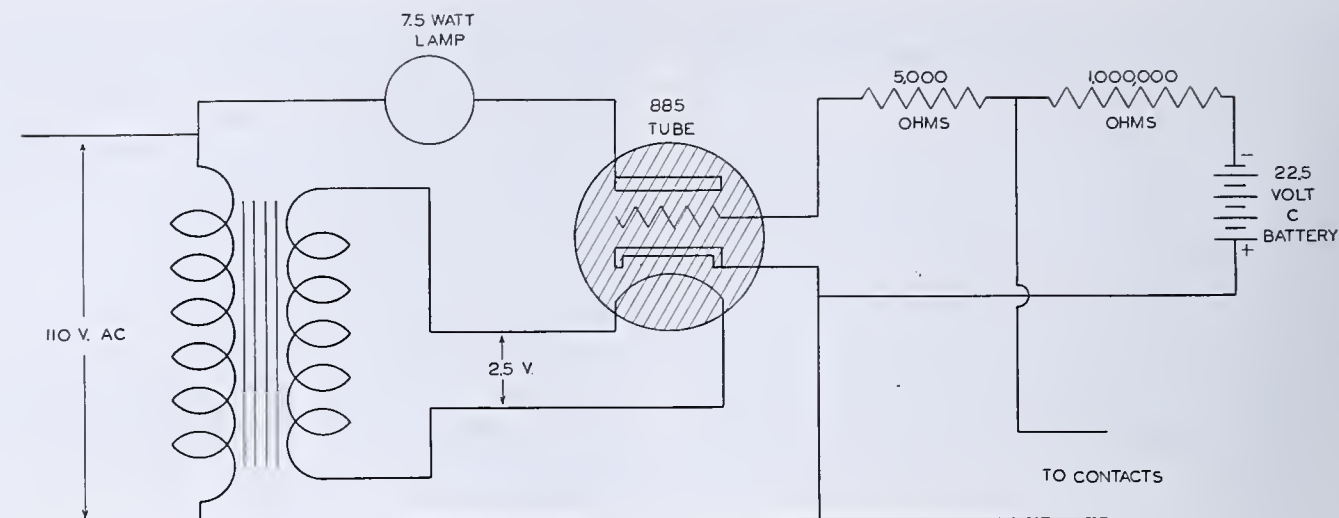


FIGURE 2. THYRATRON RELAY CIRCUIT

ference is, of course, zero. Table I shows the magnitude of the error when  $l$  is 25 and 52.5 cm. (10 and 21 inches). The 52.5-cm. (21-inch) length was used in the two manometers that have been constructed.

If the accuracy with which readings are to be made is limited to  $\pm 0.01$  mm., the length,  $l$ , must be 90 cm. (36 inches) or more. On the other hand, shorter lengths can be used, provided a proper correction is made. In the instruments that have been used in this laboratory, a length of approximately 52.5 cm. (21 inches) has been used and corrections have been applied for pressures between 2 and 2.5 cm. (0.8 and 1.0 inch) of water.

### Construction

A length of 13-mm. glass tubing is bent to form a flat U-tube 52.5 cm. (21 inches) across and 10 cm. (4 inches) high. Each arm of the U-tube is provided with a short length of 7-mm. tubing for rubber tubing connections. The glass tubing is held in a frame mounted on a flat plate, which is, in turn, supported by three leveling screws. One arm of the U-tube is held in a swivel joint by means of a clamp around the tubing. The other arm carries a small flat plate clamped to the upright section. In operation this plate rests on the top of the micrometer screw. About 15 cm. (6 inches) from this end of the instrument, two vertical guides are provided to prevent horizontal movement.

The position—i. e., the height—of the movable arm is controlled and indicated by a micrometer screw graduated in millimeters to 0.01 mm. A platinum wire is sealed into the cross arm; a second platinum wire is sealed through the center of the top of the movable arm and extends downward about 5 cm. (2 inches). The end of this platinum wire is sharpened to a very fine point, so that a point contact can be made with the center of the meniscus. These two electrodes are connected to a sensitive Thyatron relay which operates a small incandescent bulb and is so sensitive that the conductivity of tap water, or distilled water containing a few parts per million of salt, is great enough to operate it. Thus it is possible to use water with a density of one and obtain readings directly in millimeters of water.

The construction of the manometer is shown in detail in Figure 1. The two platinum contact electrodes are connected to the contacts of a Thyatron relay circuit shown in Figure 2. This circuit is similar to the ordinary Thyatron relay except that a low-power tube is used to activate an indicating lamp. The relay circuit is included for the convenience of those who do not have it readily available.

### Operation

In operation, a zero point is first determined by noting the reading on the micrometer screw when it is slowly lowered until the pointed platinum wire just touches the surface of the meniscus, causing the lamp on the relay to light. This zero point is found with both ends of the manometer open to the air. The manometer is then connected across the desired pressure differential with the high-pressure side connected to the movable arm. The micrometer screw is carefully lowered until the light flashes on, and the new reading is taken. The difference between the zero and final readings gives the pressure directly in millimeters of water. All readings must be made in the same way, with the

micrometer screw advancing in the same direction, so that contact is always made between the pointed platinum wire and the surface of the water. There is a difference of a few hundredths of a millimeter between the "make" and the "break" points. It has been suggested that this difference might be used to measure the surface tension of the liquid if a larger platinum wire were used, but no experimental work of this nature has been done.

TABLE I. ERROR

Pressure Inches of Water	Error			
	$l = 10$ inches		$l = 21$ inches	
	Inch	Mm.	Inch	Mm.
0.2	0.0	0.0	0.0	0.0
0.4	0.0003	0.0076	0.0	0.0
0.6	0.0010	0.0254	0.0002	0.0051
0.8	0.0026	0.0660	0.0004	0.0102
1.0	0.0050	0.1270	0.0011	0.0280

The manometer is very simple to use and no eyestrain is involved in reading it. The operator does not watch either the manometer or the micrometer screw, and merely needs to place the relay in some position in his line of vision. After the correct level is located very roughly, the screw is backed off until contact is broken and is again advanced very slowly until contact is just made. In this manner duplicate readings of the same pressure may be obtained in 1 or 2 minutes, depending on the operator's familiarity with the instrument. The micrometer screw is read as simply as an ordinary micrometer caliper and can be obtained from any concern manufacturing micrometer calipers.

Several other applications of this principle to the measurement of liquid levels are possible. The only requirement that must be observed is that the liquid have a moderate conductivity. The sensitivity of the relay can be altered over a wide range by slight changes in the circuit and by the use of other tubes. With the present equipment the relay will operate using methyl alcohol containing 1 drop of hydrochloric acid in 200 cc. Many other liquids can undoubtedly be used if a very small amount of an electrolyte is added. The change in level of a liquid in an accurately machined cylinder caused by the addition of solids of odd shapes could be determined with extreme accuracy for volume or density determinations of granular solids. In addition, it should be possible to measure the thickness of fluid films fairly accurately, provided they are not below the range of accuracy of the micrometer screw.

### Acknowledgment

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# A Catalytic Color Reaction for Tungsten

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**T**UNGSTEN markedly catalyzes the reaction between titanous chloride and malachite green which normally proceeds very slowly at room temperature in a dilute acid solution. Sexivalent tungsten is rapidly reduced by titanous chloride to lower valence states which quickly reduce malachite green to the leuco form.

In investigating this catalyzed reaction from the standpoint of the detection of tungsten, the following procedure was adopted. Five-hundredths milliliter of approximately 5 per cent titanous chloride solution (freshly prepared by diluting LaMotte's 20 per cent titanous chloride with water) was added to the sodium tungstate solution, containing any added foreign substance and having a volume of 1.9 ml. After one minute this solution was quickly added to 0.10 ml. of 0.02 per cent aqueous malachite green solution contained in a small vial, and the time noted for the bluish green or yellow color (depending upon the acidity) of the solution to fade to colorless or the very pale violet of titanous ions.

Figure 1 shows the relation between tungsten concentration and reaction time at two acidities—first, when the solution contained no acid other than that in the titanous chloride (curve A), and second, when 0.10 ml. of 2 *N* hydrochloric acid was added to the reaction mixture which had a final volume of 2.0 ml. (curve B). In the first case the pH of the reaction mixture was approximately 2 (the acidity corresponded to that of a solution containing 0.015 ml. of 2 *N* hydrochloric acid in 2 ml. of water), and in the second case the pH was approximately 1. These experiments were carried out at 25° C. The concentration of the approximately 5 per cent titanous chloride solution was determined by titration with ferric iron and found to be 0.32 *N*.

It was found that tin, arsenic, antimony, bismuth, copper, gold, platinum, lead, thallium, iron, vanadium, uranium, and columbium did not catalyze the reaction between malachite green and titanous chloride. Molybdenum does catalyze the reaction, but its effect is much less marked than that of tungsten (Table I, Nos. 28 to 31). The effect of foreign sub-

stances on the tungsten-catalyzed reaction may be seen from the results in Table I. These experiments were made at room temperature (23° to 28° C.). Alkali chlorides and chlorides of metals which are not reduced by trivalent titanium do not interfere seriously with the reaction; but the reaction time of the blanks is in general decreased. Alkali sulfates markedly increase the reaction velocity between malachite green and trivalent titanium in the absence of tungsten, and decrease the catalytic effect of tungsten. Magnesium sulfate behaves like the alkali sulfates, but zinc sulfate causes but little change.

TABLE I. EFFECT OF FOREIGN SUBSTANCES ON TUNGSTEN-CATALYZED MALACHITE GREEN-TITANOUS CHLORIDE REACTION  
(Total volume of reaction mixture 2 ml. in each case)

No.	Addition	Reaction Time	
		0.01 mg. W present Min.	Blank Min.
1	.....	0.2-0.3	60
2	0.05 ml. 2 <i>N</i> HCl	0.6-0.8	...
3	0.1 ml. 2 <i>N</i> HCl	1 -1.8	8
4	0.1 gram NaCl	0.3	13
5	0.1 gram NaCl + 0.1 ml. 2 <i>N</i> HCl	2	8
6	0.1 gram NH <sub>4</sub> Cl	0.2	15
7	0.1 gram NH <sub>4</sub> Cl + 0.1 ml. 2 <i>N</i> HCl	2	10
8	0.1 gram Na <sub>2</sub> SO <sub>4</sub>	0.5	2
9	0.1 gram Na <sub>2</sub> SO <sub>4</sub> + 0.1 ml. 2 <i>N</i> HCl	2.3	4
10	0.1 gram MgCl <sub>2</sub> ·6H <sub>2</sub> O + 0.1 ml. 2 <i>N</i> HCl	1.3	10
11	0.1 gram MgSO <sub>4</sub> ·7H <sub>2</sub> O	0.2	1.3
12	0.1 gram MgSO <sub>4</sub> ·7H <sub>2</sub> O + 0.1 ml. 2 <i>N</i> HCl	2.5	5
13	0.1 gram CaCl <sub>2</sub>	0.2	8
14	0.1 gram CaCl <sub>2</sub> + 0.1 ml. 2 <i>N</i> HCl	1.3	6
15	0.1 gram MnCl <sub>2</sub> ·4H <sub>2</sub> O	1.2	8
16	0.1 gram ZnSO <sub>4</sub> ·7H <sub>2</sub> O + 0.1 ml. 2 <i>N</i> HCl	0.8	15
17	0.1 gram AlCl <sub>3</sub> ·6H <sub>2</sub> O + 0.1 ml. 2 <i>N</i> HCl	0.3	10-15
18	0.05 gram SnCl <sub>2</sub> ·2H <sub>2</sub> O + 0.1 ml. 2 <i>N</i> HCl	0.8	12
19	0.5 mg. Fe <sup>+++</sup> as ferric alum + 0.1 ml. 2 <i>N</i> HCl <sup>a</sup>	1	7
20	5 mg. Fe <sup>+++</sup> as ferric alum + 0.1 ml. 2 <i>N</i> HCl <sup>a</sup>	5	5
21	50 mg. FeSO <sub>4</sub> ·7H <sub>2</sub> O + 0.1 ml. 2 <i>N</i> HCl	0.6	10
22	0.1 mg. VV as NH <sub>4</sub> VO <sub>3</sub> <sup>b</sup>	6	11
23	0.1 mg. VV as NH <sub>4</sub> VO <sub>3</sub> + 0.1 ml. 2 <i>N</i> HCl <sup>b</sup>	2	15
24	0.25 mg. UVI as UO <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> + 0.1 ml. 2 <i>N</i> HCl <sup>c</sup>	3	15
25	0.5 mg. TiI as TiCl <sub>3</sub>	0.2	>30
26	1 mg. Pb as PbCl <sub>2</sub>	1.7	>30
27	0.1 mg. Cb <sub>2</sub> O <sub>5</sub> + 0.05 ml. 2 <i>N</i> HCl	0.3	7
28	0.02 mg. MoVI as ammonium molybdate + 0.1 ml. 2 <i>N</i> HCl	1	8
29	0.05 mg. MoVI as ammonium molybdate + 0.1 ml. 2 <i>N</i> HCl	1	6-7
30	0.1 mg. MoVI as ammonium molybdate + 0.1 ml. 2 <i>N</i> HCl	0.9	5
31	0.5 mg. MoVI as ammonium molybdate + 0.1 ml. 2 <i>N</i> HCl	0.2	1
32	1 mg. (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + 0.1 ml. 2 <i>N</i> HCl	0.1	5
33	5 mg. (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + 0.1 ml. 2 <i>N</i> HCl	0.1	0.8
34	10 mg. NaF	1	...
35	10 mg. NaF + 0.1 ml. 2 <i>N</i> HCl	4	10
36	5 mg. tartaric acid + 0.1 ml. 2 <i>N</i> HCl	...	7
37	10 mg. tartaric acid	...	0.0
38	10 mg. tartaric acid + 0.1 ml. 2 <i>N</i> HCl	1.2	3.5

<sup>a</sup> 0.05 ml. of 5% TiCl<sub>3</sub> added in excess over amount required to reduce Fe<sup>III</sup>.  
<sup>b</sup> 0.08 ml. of 5% TiCl<sub>3</sub> added. <sup>c</sup> 0.10 ml. of 5% TiCl<sub>3</sub> added.

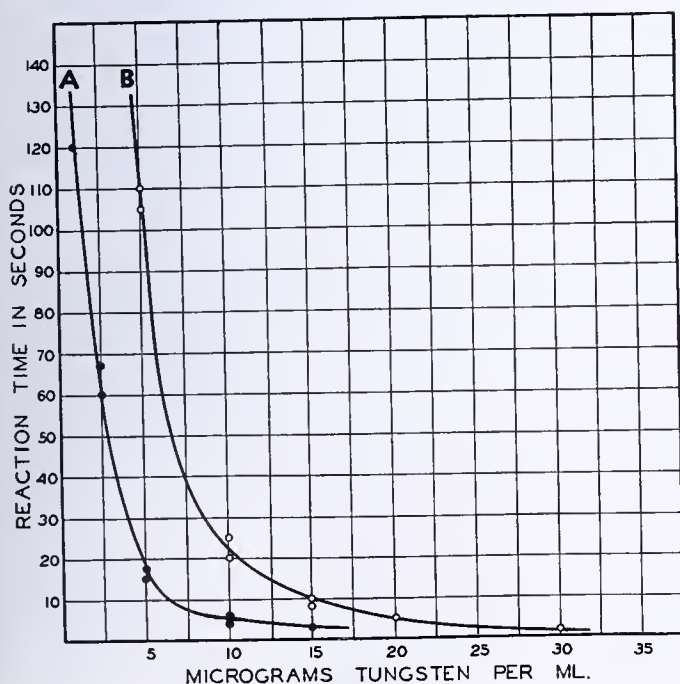


FIGURE 1. RELATION BETWEEN TUNGSTEN CONCENTRATION AND REACTION TIME  
A. pH about 2; B. pH about 1

The effect of sulfate in increasing the reaction rate in the absence of tungsten is perhaps to be explained by the formation of a complex sulfate with quadrivalent titanium and the consequent increase in the reduction potential of the titanous-titanic system. Nitrates must not be present because they are of course reduced by titanous ion. Tartaric acid greatly increases the reaction velocity in the absence of tungsten, especially when the acidity is low. With no added hydrochloric acid, malachite green is instantaneously decolorized by titanous chloride when a small amount of tartaric acid (0.5 per cent or less) is present. This corresponds to the conditions under which various dyes are ordinarily titrated with titanous chloride. Phosphate accelerates the reaction between malachite green and titanous chloride in 0.1 *N* hydrochloric acid, in both the absence and presence of tungsten. Fluoride forms a complex with tungsten and inhibits the catalysis.



Table I shows that when reducible metal ions such as  $\text{Fe}^{+++}$  and  $\text{UO}_2^{++}$  are present, and an amount of titanous chloride is added which is sufficient to reduce the metal to a lower valence state and leave an excess of titanous ion, the catalyzed reaction proceeds much more slowly than in the absence of the reducible metals. Accordingly the detection of tungsten by the method described fails when appreciable amounts of such metals as  $\text{Fe}^{\text{III}}$ ,  $\text{U}^{\text{VI}}$ , and  $\text{V}^{\text{V}}$  are present. Cations which are reduced to the metal or form insoluble chlorides ( $\text{Ag}$ ,  $\text{Hg}$ ,  $\text{Au}$ ,  $\text{Pt}$ , etc.) must of course be absent.

Although molybdenum catalyzes the reaction, as already mentioned, its effect is much less than that of tungsten, so that in small amounts it hardly interferes (Nos. 28 to 30, Table I). Moreover, the presence of molybdenum is revealed by the appearance of a yellow-brown color, which fades rapidly, when titanous chloride is added to a 0.01  $N$  hydrochloric acid solution containing molybdate. When molybdenum and phosphate are simultaneously present, a permanent strong red-brown color is produced when titanous chloride is added to the acid solution, but the reduction of malachite green hardly proceeds more rapidly than in the absence of phosphate.

The catalysis described may be applied in detecting tung-

sten by the spot technic. A 0.05-ml. drop of test solution (free from the interfering substances mentioned) which may be neutral or 0.1  $N$  in hydrochloric acid is treated on a spot plate with 0.01 ml. of 1 per cent titanous chloride solution, and 0.01 ml. of 0.005 per cent aqueous malachite green solution is then added. It is important to add the titanous chloride first to the test drop, because if the malachite green is added before the titanous chloride the catalyzed reaction proceeds more slowly.

The test drop becomes colorless (very pale violet) more or less rapidly, depending upon the tungsten concentration. With one part of tungsten in 100,000 of neutral solution, the blue-green color fades in about 3 seconds, whereas with one part in 500,000 decoloration occurs in 1 to 1.5 minutes. A blank remains green for 4 to 5 minutes. A tungsten concentration of 1 to 500,000 may, under these conditions, be considered the limit of the reaction, because at a concentration of 1 to 1,000,000 decoloration requires 3 minutes. When the test drop is 0.1  $N$  in hydrochloric acid, the limiting concentration may be set at 1 to 250,000 (decoloration in 2 to 3 minutes, blank remains colored 3.5 to 4 minutes).

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## Buret Top for Precise Control of the Rate of Outflow

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IT IS GENERALLY recognized that tapless burets have many advantages over those with small taps at the lower end. Several methods of controlling the flow of liquid in tapless burets have been developed, notably that of Schilow (2-5) in which a manometer is used, and that of Benedetti-Pichler (1, 3) which employs a capillary to break the flow and a small clip on rubber tubing to stop the flow. The accuracy of control of the latter buret was found to be limited by movement of the rubber tubing and by alteration in the position of the clip; the present paper deals with a buret top, which, while using the basic principle of Benedetti-Pichler's method, allows a much greater exactness of control.

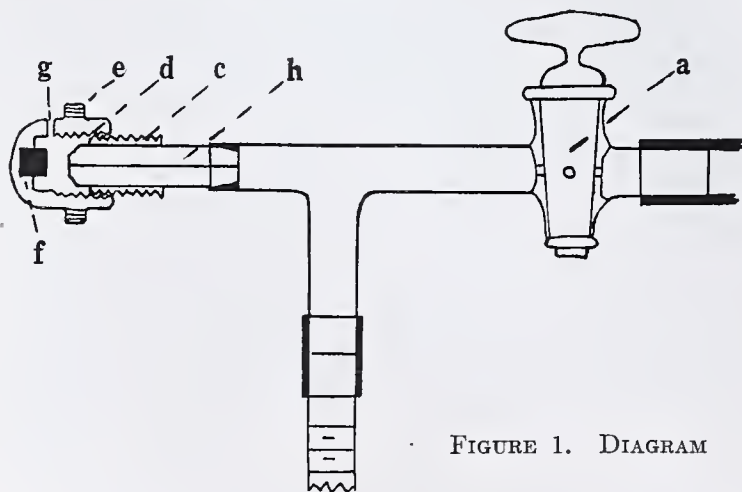


FIGURE 1. DIAGRAM

The actual buret tube used was a 5-ml. graduated pipet drawn out at the bottom to a jet delivering about 0.015-ml. drops, and ground flat at the top. Equally satisfactory control was obtained using 10-ml. or 1-ml. tubes. The buret top consists of a T-tube with the end of its vertical arm ground flat and fitted closely to the tube by rubber tubing. A full-scale section of the buret top is shown in Figure 1.

On one side of the horizontal arm is a tap,  $a$ ; filling is done by closing the regulator and opening this tap, which connects to low pressure from a filter pump. Into the other side of the T-tube is ground, and cemented with sealing-wax, a fine-bore heavy

capillary tube,  $h$ , ground smooth and beveled at its free end. On this is cemented a threaded collar,  $c$ , having 30 turns per 2.5 cm. (1 inch), screwing into a brass cap,  $d$ , turned from solid rod and having a raised milled portion,  $e$ . Into a small depression inside the end of the cap fits a cylindrical pad of firm rubber,  $f$ , having its projecting end perfectly flat, while a fine hole,  $g$ , through the brass wall allows free entry of air. A slight turn of the regulating mechanism alters the pressure of the pad on the capillary tip, giving a very accurate control of the liquid flow. As the jet of the buret was always kept in the solution being titrated, this fine control allowed a very smooth approach to the end point impossible with a tap-type buret.

This buret has been used for routine work on halogenation, involving iodine-thiosulfate titrations; the precision of the titer was determined by the accuracy to which the tube could be read, and by the sensitivity of the indicator. Discrepancies introduced by these two factors were far greater than any due to the control mechanism. Using a 5-ml. tube and lighting from a small bulb behind thin paper at the back of the scale, the titers were repeatable to 0.01 ml., and with reasonable care an approximation to the third place could be obtained.

The device proved useful for the accurate adjustment of the liquid level in micropipets, especially if dangerous liquids were being handled. A further very practical use was found in low-pressure distillation; the buret top was used in place of the traditional screw clip on rubber tubing at the top of the fine capillary tube dipping into the liquid. With this control the pressure could be adjusted rapidly to any desired level, and could be kept reasonably constant throughout the distillation.

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RECEIVED August 13, 1938.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



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## Analysis of Sugar Mixtures Containing Dextrose, Levulose, Maltose, and Lactose

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**D**URING the past few years methods for the determination of dextrose and levulose in sugar products have been studied in this laboratory. A procedure applicable to raw cane sugars has been published (17, 18), and likewise one for cane molasses (5). Some food products also contain maltose and lactose, and the investigation has been extended to include these sugars as well. Sucrose can be estimated in the presence of the other four sugars by means of invertase, and for this reason only the four reducing sugars are considered in this article.

With such complex sugar mixtures it is usually necessary to resort to combined methods, as has been pointed out by Browne (2, 3), because there are few reactions which permit the quantitative separation of one sugar from all the others. Selective fermentation with specific organisms has been employed successfully by a number of investigators, but the necessary pure cultures are not always readily available, they require painstaking technique in their propagation and application, and in the usual chemical laboratory used for sugar analysis it is difficult to prevent contamination.

Chemical methods have lately become available for the selective determination of levulose and of monosaccharides, and have been applied to the analysis of sugar mixtures. This suggested their possible use in the analysis of mixtures of the four sugars in question.

### Principle of the Method

The determination of four sugars by combined methods requires four equations. In the absence of salts and organic impurities the total solids or the polarization may serve as criteria, but such cases are rare in practice, and it is generally necessary to depend on methods that are less affected by accompanying impurities. Lactose is the only sugar among the four that can be determined independently. It may either be oxidized to mucic acid and weighed in this form, or else the other three sugars may be removed by fermentation with yeast, and the residual lactose estimated by any suitable method. The dextrose and levulose may be determined by combining Jackson and Mathews' modification of the Nijns method (8) for the selective determination of levulose with the method of Steinhoff (14) for the selective determination of monosaccharides in the presence of disaccharides by means of a modified Barfoed reagent. The total reducing sugars are found with Fehling solution.

If  $G$  = mg. of dextrose (glucose)  
 $F$  = mg. of levulose (fructose)  
 $M$  = mg. of maltose hydrate  
 $L$  = mg. of lactose hydrate  
 $R_1$  = mg. of apparent levulose by the method of Jackson and Mathews  
 $R_2$  = mg. of dextrose plus levulose, expressed as levulose, by the copper acetate method of Steinhoff  
 $R_3$  = mg. of total reducing sugars, expressed as dextrose, by Fehling solution

then

$L$  is determined separately (1)

$$R_1 = 0.0806 G + F \quad (2)$$

$$R_2 = aG + F \quad (3)$$

$$R_3 = G + bF + cM + dL \quad (4)$$

The factor 0.0806 in Equation 2 is the reducing ratio of dextrose to levulose (12.4 mg. of dextrose have the same reducing power as 1 mg. of levulose). Factor  $a$  is the reducing ratio of dextrose to levulose in Steinhoff's acetate method, and  $b$ ,  $c$ , and  $d$  are the reducing ratios of levulose, maltose, and lactose, respectively, to dextrose for Fehling solution. The values of  $a$ ,  $b$ ,  $c$ , and  $d$  vary with the concentration, and are found from tables.

By solving Equations 2 and 3 for  $G$  and  $F$ , we find

$$G = \frac{R_2 - R_1}{a - 0.0806}$$

and

$$F = R_2 - aG$$

$L$ ,  $G$ , and  $F$  being known, Equation 4 gives

$$M = \frac{R_3 - (G + bF + dL)}{c}$$

If the disaccharides had no reducing effect whatever on the reagents employed for the determination of the monosaccharides, as claimed by the original authors of the methods, the procedure and the calculation of the results would be simple. But it has been found that both maltose and lactose have a slight reducing effect on the Jackson and Mathews reagent, as well as on the Steinhoff copper acetate reagent. This subject, and the procedure for applying the necessary corrections are discussed below.

### Determination of Lactose

The writers first tried the mucic acid method of Tollens, Kent, and Creydt (4, 9), as modified by van der Haar (6). The method lacks precision, as stated by van der Haar him-



self, differences of as much as 8 mg. of mucic acid being sometimes obtained in duplicate determinations. It is not very accurate either and usually gives low results in the presence of other sugars or nonsugars. The galactose, found from van der Haar's Table I and multiplied by 2, should give lactose hydrate, but experiments by the writers with known sugar mixtures have given an average factor of 2.2. With low percentages of lactose in the mixture the method gives fairly satisfactory results, sufficiently exact for practical purposes but it is not recommended.

The method finally adopted is a modified form of the fermentation procedure of Hoffman, Schweitzer, and Dalby (7).

The sample is placed in a 500-ml. volumetric flask, and a thin suspension of a mixture containing 35 grams of compressed bakers' yeast, 0.5 gram of ammonium sulfate, and 0.2 gram of sodium bisulfite in water is added. The mixture in the flask is further diluted with water to a volume of about 400 ml. The flask is closed with a stopper provided with a delivery tube, the outer end of which is immersed 1 cm. below the surface of water in a beaker. The flask is placed in a water bath or thermostat kept at 30° C., and it is shaken from time to time.

After standing a minimum of 4 hours, 15 ml. of a 20 per cent solution of neutral lead acetate are added, and the volume is made up to the mark at 20° C. Next, 1 gram of Filter-Cel is added, and the contents of the flask are thoroughly shaken and filtered through a folded quantitative filter paper. The first, turbid portion of the filtrate is discarded, and exactly 200 ml. of the clear filtrate are collected in a dry volumetric flask calibrated for 200- and 220-ml. contents. To the 200-ml. solution 15 ml. of a phosphate-oxalate solution are added, prepared by dissolving 7 grams of disodium phosphate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) and 3 grams of potassium oxalate ( $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) to 100 ml. The flask is made up to the 220-ml. mark at 20° C., 0.5 gram of Filter-Cel is added, and the contents are shaken vigorously. The solution is filtered through a quantitative filter paper, and the clear filtrate is collected for the sugar determination. Lactose can be determined by any of the standard methods, such as the Munson and Walker method used by the writers.

The fermentation method should be carried out with a reliable brand of yeast, and its fermenting power should be checked by appropriate tests. Blank tests run with a good yeast usually yield very low reduction values, and the results are not trustworthy for corrections. It is a much better practice to use pure lactose for the purpose. It is therefore recommended to run parallel determinations with lactose alone, or with a known sugar mixture approximating that of the sample.

To give an example, 1.056 grams of lactose were treated in the 500-ml. flask. After the fermentation, 200 ml. of the filtrate, containing 0.4224 gram of lactose, were made up to 220 ml., and of the final filtrate 50 ml., containing 96 mg. of lactose, were used for the sugar determination. Found, 0.1622 and 0.1601 gram of cupric oxide; average, 0.1612 gram of cupric oxide, corresponding to 128.8 mg. of copper and 97.5 mg. of lactose hydrate. In another experiment a mixture of 1.056 grams of lactose, 0.704 gram each of maltose and dextrose, and 0.176 gram of levulose was similarly treated, and there was obtained 0.1626 and 0.1621, an average of 0.1624 gram of cupric oxide, corresponding to 98.2 mg. of lactose hydrate. The higher result is due in part to the volume occupied by the yeast and the lead precipitates in the flasks, and in the second case possibly to unfermented reducing substances. A corresponding correction must be applied to the result obtained upon the sample analyzed.

### Determination of the Apparent Levulose

This is carried out according to the directions of Jackson and Mathews (8). It has been found by the writers that both maltose and lactose reduce the copper carbonate reagent. The reducing effect is smaller than that of dextrose, but much larger than that of sucrose. It varies not only with the concentration of these sugars alone, being relatively greater for higher concentrations of them, but also with the concentration of dextrose and levulose present in mixtures, the reducing power also increasing with the total sugar concentration. The variations are small, however, and for practical purposes

average figures may be used to correct for the reducing effect of maltose and lactose. An average of 26.0 mg. of maltose hydrate and 25.6 mg. of lactose hydrate was found to be equivalent to 1 mg. of levulose.

### Determination of Dextrose Plus Levulose

The reduction method of Steinhoff has been retained with only slight changes, but the estimation of the reduced copper had to be modified. Steinhoff acidifies the reaction mixture while it is still hot, and immediately adds standard iodine solution. After cooling, the excess iodine is titrated back with standard thiosulfate. This procedure leads to uncertain results because the iodine added to the hot solution is partly volatilized. The writers have therefore adopted the iodometric method of Shaffer and Hartmann (12), modifying it to suit the particular conditions.

The following reagents are used:

Sodium acetate solution, prepared by dissolving 500 grams of the crystallized salt ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ) in about 800 ml. of hot water, cooling, and making up to 1 liter.

Sulfuric acid, about 2 *N*, prepared by diluting 57 ml. of concentrated acid to 1 liter.

Potassium iodide-iodate solution, prepared by dissolving 5.4 grams of potassium iodate and 60 grams of potassium iodide to a total volume of 1 liter. The solution is made alkaline by adding 0.25 gram of sodium hydroxide dissolved in a little water before completing the volume.

Saturated solution of potassium oxalate, prepared by dissolving 165 grams of the hydrated salt ( $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) in 500 ml. of hot water, and cooling to room temperature.

0.1 *N* thiosulfate solution, exactly standardized by iodometric determination with potassium dichromate.

Soxhlet copper sulfate solution (Fehling I), prepared according to the directions of the Association of Official Agricultural Chemists (1).

TABLE I. COPPER ACETATE REAGENT

(Milligrams of dextrose or levulose corresponding to varying volumes of 0.1 *N* thiosulfate solution; reducing ratios for varying proportions between levulose and dextrose)

Thio- sulfate Ml.	$R_2$		Reducing Ratios, $\alpha$			
	Dex- trose Mg.	Levu- lose Mg.	100 levulose 0 dextrose	75 levulose 25 dextrose	50 levulose 50 dextrose	25 levulose 75 dextrose
1	5.0	3.2	0.640	0.556	0.829	0.852
2	7.0	5.8	0.829	0.803	0.933	0.956
3	9.0	8.3	0.922	0.952	0.976	1.000
4	11.1	10.7	0.964	1.000	0.981	1.013
5	13.3	12.9	0.970	0.980	0.955	1.010
6	15.5	14.9	0.961	0.953	0.930	0.984
7	17.8	16.8	0.944	0.914	0.905	0.957
8	20.3	18.6	0.916	0.897	0.880	0.931
9	22.9	20.3	0.886	0.870	0.855	0.906
10	25.7	22.1	0.860	0.845	0.830	0.880
11	28.7	23.9	0.833	0.819	0.805	0.853
12	31.8	25.7	0.808	0.793	0.780	0.825
13	35.4	27.7	0.782	0.767	0.755	0.797
14	39.0	29.4	0.754	0.747	0.730	0.769
15	43.3	31.4	0.726	0.715	0.706	0.740
16	47.9	33.6	0.701	0.688	0.681	0.711
17	53.3	35.8	0.672	0.666	0.656	0.681
18	59.5	38.4	0.645	0.640	0.631	0.651
19	66.6	40.9	0.612	0.595	0.605	0.621
20	74.6	43.8	0.587	0.583	0.581	0.593
21	84.1	46.9	0.558	0.555	0.555	0.564
22	95.0	50.5	0.532	0.530	0.529	0.536

Ten milliliters of the copper sulfate solution and 20 ml. of the sodium acetate solution are pipetted into a 250-cc. wide-mouthed Erlenmeyer flask, and a measured amount of the sugar solution is added. The quantity of sugar solution must be such that the thiosulfate corresponding to the copper reduced is within the limits of Table I, and that the thiosulfate corresponding to the copper reduced from Fehling solution by the same quantity of sugar solution is within the limits of Table II. A few preliminary experiments are usually necessary to ascertain the optimum amount for both determinations.

After the sugar solution has been added, the volume is completed to a total of 50 ml. by the addition of water. After



thorough mixing, the Erlenmeyer is closed with a rubber stopper provided with a Bunsen valve, to prevent reoxidation of the reduced copper. The solution is placed in a briskly boiling water bath, the stop watch started, and the flask removed from the bath after exactly 20 minutes. It is then quickly cooled to room temperature under a water tap. During this time the Bunsen valve must be vented from time to time to prevent boiling caused by the vacuum. After cooling, 25 ml. of the iodide-iodate solution are carefully added from a pipet and mixed with the solution by gentle shaking. Then 40 ml. of the 2 *N* sulfuric acid are run in rapidly from a measuring cylinder, the flask being rotated to wash down the inside wall. This is followed by the addition of 20 ml. of the potassium oxalate solution from a measuring cylinder. The contents of the flask are well mixed until the precipitate is completely dissolved, and the excess iodine is titrated with the standard thiosulfate.

A blank is run with water instead of sugar solution. The difference between the thiosulfate titer of the blank and that of the sample is a direct measure of the cuprous oxide precipitated.

TABLE II. COPPER TARTRATE REAGENT

(Milligrams of dextrose corresponding to varying volumes of thiosulfate solution, and reducing ratios of levulose, maltose, and lactose, with respect to dextrose)

Thiosulfate Ml.	<i>R</i> <sub>3</sub> , Dextrose Mg.	Reducing Ratios		
		Levulose, <i>b</i>	Maltose hydrate, <i>c</i>	Lactose hydrate, <i>d</i>
1	2.2	0.648	0.394	0.499
2	5.3	0.815	0.481	0.616
3	8.5	0.868	0.508	0.653
4	11.6	0.893	0.521	0.669
5	14.8	0.907	0.528	0.678
6	18.0	0.914	0.532	0.683
7	21.2	0.918	0.535	0.685
8	24.4	0.921	0.537	0.686
9	27.6	0.922	0.538	0.689
10	30.8	0.922	0.538	0.685
11	34.0	0.921	0.538	0.684
12	37.2	0.920	0.538	0.683
13	40.5	0.918	0.537	0.681
14	43.7	0.917	0.537	0.679
15	47.0	0.914	0.536	0.677
16	50.2	0.912	0.536	0.675
17	53.5	0.910	0.536	0.672
18	56.8	0.907	0.534	0.670
19	60.0	0.904	0.533	0.668
20	63.3	0.895	0.531	0.665
21	67.1	0.897	0.534	0.668
22	71.3	0.901	0.540	0.673
23	75.5	0.905	0.545	0.678
24	80.0	0.910	0.551	0.685
25	85.1	0.915	0.561	0.695

Results of duplicate determinations usually check within 0.1 to 0.2 ml. of thiosulfate. But larger discrepancies occur occasionally, due to the following causes:

Differences in buret drainage, because of the relatively larger amounts of thiosulfate run out and the greater speed of their removal in blank determinations, may cause an error amounting to 0.15 ml.

A difference of one drop in the quantity of the iodide-iodate solution pipetted out causes an error of as much as 0.15 ml. of thiosulfate, and for this reason the emptying of the pipet must be carefully standardized.

The end point, determined with starch solution, while sharp, is affected by light conditions. It is best to use a daylight lamp, and to prepare a blank solution of the copper reagent for comparison.

The precipitate must be completely dissolved before the titration with thiosulfate. Without this precaution there may be fading of the end point, indicating incomplete solution.

The boiling water in the bath causes a certain amount of agitation of the contents of the flasks, and variations in this factor affect the results. The water must be boiling briskly in all parts of the bath. It may be preferable to use a constant-temperature bath kept at 100° C. by the use of a higher boiling liquid, and to agitate the flasks mechanically.

If the Erlenmeyer flasks are not thoroughly clean, the copper precipitate tends to creep up on the walls. To prevent this, the flasks should be cleaned regularly with chromic acid mixture.

The reducing effect of dextrose and levulose, obtained from the National Bureau of Standards, and of mixtures of the two, on the copper acetate reagent was determined, and the results are shown in Table I, which gives the milligrams of

dextrose or levulose equivalent to the number of milliliters of thiosulfate found, and also the values of the factor *a* in Equation 3, for varying proportions between the two sugars.

### Determination of Total Reducing Sugars

In this determination, 10 ml. of Soxhlet copper sulfate solution (Fehling I) and 10 ml. of alkaline tartrate solution (Fehling II), both prepared according to the directions of the Association of Official Agricultural Chemists (1), are mixed in a 250-cc., wide-mouthed Erlenmeyer flask. The same quantity of sugar solution as was used in the determination of dextrose plus levulose is added, the volume is made up to a total of 50 ml., and the analysis is carried out exactly as described for that determination, except that only 25 ml. of the 2 *N* sulfuric acid are used instead of 40 ml.

The reducing effect on the copper tartrate reagent has been measured for dextrose, levulose, maltose, and lactose. The results are shown in Table II, which gives the milligrams of dextrose corresponding to varying milliliters of 0.1 *N* thiosulfate solution, and the values of the factors *b*, *c*, and *d* (reducing ratios of levulose, maltose hydrate, and lactose hydrate with respect to dextrose) in Equation 4. These reducing ratios are very close to those for the Munson and Walker method, as would be expected.

### Reducing Power of Mixtures of Sugars

Two hypotheses have been used to account for the combined reducing effect of sugars present in mixtures. One of these assumes that the reducing effect is an additive property—for example, the copper reduced by a mixture of *a* mg. of dextrose and *b* mg. of levulose is expected to be the sum of the copper reduced by *a* mg. of dextrose and *b* mg. of levulose, each present alone. Schwartz (11) found, however, that the reducing power of mixtures is governed by a rule analogous to that observed by Vosburgh (16) for the specific rotation of sugar mixtures. This rule states that the specific rotations in a mixture of two sugars are equal to the specific rotations which each sugar would have if present at the total sugar concentration. Similarly, the amount of copper reduced by *a* mg. of invert sugar is the sum of one-half of the copper reduced by *a* mg. of dextrose and one-half of the copper reduced by *a* mg. of levulose. This "fractional proportionality" rule is illustrated by the following example from the reduction tables of Quisumbing and Thomas (10):

	Copper Mg.
200 mg. of invert sugar alone	372.1
100 mg. of dextrose alone reduce	201.2
100 mg. of levulose alone reduce	185.0
200 mg. of invert sugar, according to the simple additive rule, would reduce	386.2
200 mg. of dextrose reduce	386.0
200 mg. of levulose reduce	360.6
One-half of copper reduced by 200 mg. of dextrose equals	193.0
One-half of copper reduced by 200 mg. of levulose equals	180.3
200 mg. of invert sugar, according to the fractional proportionality rule, would reduce	373.3

The last figure checks within 1.1 mg. with the copper actually found, while the simple additivity rule gives 14.1 mg. of copper too much.

Analogously, the amount of copper reduced by a mixture of 50 mg. of dextrose and 150 mg. of levulose equals the sum of one-quarter of the copper reduced by 200 mg. of dextrose and three-quarters of the copper reduced by 200 mg. of levulose.

The simple additivity rule has been found to give correct results, within the limits of error, in those cases where the reducing effect of one sugar is very small with respect to that of another, as, for instance, for mixtures of levulose and dextrose analyzed by the method of Jackson and Mathews. The frac-



tional proportionality rule is of more general application and gives results close to the truth when the reducing power of one sugar does not greatly differ from that of another sugar, as when a mixture of dextrose and levulose is analyzed with Fehling solution. But larger errors are produced when the reducing power of one sugar differs materially from that of another. This applies to the analysis of mixtures of dextrose and levulose by the Steinhoff acetate reagent, and of mixtures of a monosaccharide and a disaccharide by means of Fehling solution. This may be seen from Table III.

TABLE III. REDUCING POWER OF MIXTURES

		Thiosulfate		Caled. by
Steinhoff Acetate Reagent		Found	Caled. by additivity rule	fractional proportionality rule
Dextrose	Levulose			
Mg.	Mg.	Ml.	Ml.	Ml.
50	50	18.76	21.36	19.13
12.5	37.5	20.28	22.29	21.25
37.5	12.5	17.60	18.40	18.02
Steinhoff Tartrate Reagent		Found	Caled. by additivity rule	fractional proportionality rule
Dextrose	Maltose			
10	70	15.12	15.58	15.05
20	60	16.46	17.10	16.33
30	50	17.84	18.53	17.61
40	40	19.24	19.93	18.89
50	30	20.51	21.28	20.16
60	20	21.70	22.59	21.44
70	10	22.73	23.51	22.72
Mixture		Found	Caled. by additivity rule	fractional proportionality rule
Levulose	Maltose			
10	70	14.33	15.11	14.83
20	60	15.70	16.42	15.89
30	50	17.00	17.64	16.94
40	40	18.27	18.75	18.00
50	30	19.47	19.78	19.05
60	20	20.48	20.76	20.11
70	10	21.47	21.56	21.16

With the Steinhoff acetate reagent, both rules give high results, but those by the fractional proportionality rule check better with those found by experiment. The differences are smaller when the ratio of dextrose to levulose is high. With mixtures of dextrose or levulose and maltose, determined by means of Fehling solution, the results found are always lower than those calculated by the additivity rule. In the case of the dextrose-maltose mixtures the differences increase with the ratio of monosaccharide to disaccharide; but in the case of the levulose-maltose mixtures the differences decrease with this ratio. The fractional proportionality rule gives smaller errors than the additivity rule, and mostly in the opposite direction. In a few instances the found values check with the theoretical within the limit of error. With a rise in the ratio of monosaccharide to disaccharide the differences first increase, and then decrease again. With a very small ratio of levulose to maltose the experimental value is well below the theoretical.

Since the reducing power of mixtures of two sugars is already a fairly complicated function of the reducing power of the components, it may be expected that the relations are much more complex when more than two sugars are present in mixtures. This entire subject requires further investigation.

At present the best and most practical procedure for analyzing mixtures of sugars by combined reduction methods is that of Browne (3), who has shown that the formulas established by him, with the use of reducing ratios, give generally reliable results. He also called attention to the fact that in some cases, as with mixtures of monosaccharides and disaccharides, the reducing ratios are not constant. It has since been found that the reducing ratios vary not only when determined for each sugar present alone, but also with the proportion between the sugars when present in mixtures. However, this circumstance can be readily taken care of by using reducing ratios found experimentally for mixtures of two

sugars in varying proportions, and this has been done in establishing Table I, for the Steinhoff acetate method. Application of the same experimental procedure to the four sugars when determined by Fehling solution would entail an immense amount of work, and it has been necessary to depend on a few check analyses of known mixtures, to test the use of Table II, which gives the reducing ratios for the various sugars when present alone. Such check analyses are shown under the heading of "Method of Calculation."

Reducing Effect of Maltose and Lactose on Steinhoff's Copper Acetate Reagent

Steinhoff stated in his paper that maltose has no reducing effect whatever on the copper acetate reagent, but the writers have not been able to confirm this, and they have found that lactose likewise reduces this reagent.

TABLE IV. CORRECTIONS

(To be applied to milliliters of thiosulfate found, for varying quantities of maltose or lactose present in addition to dextrose or levulose)

Maltose Hydrate and Dextrose				Maltose Hydrate and Levulose			
Dextrose	200 mg. maltose	100 mg. maltose	50 mg. maltose	Levulose	200 mg. maltose	100 mg. maltose	50 mg. maltose
Mg.				Mg.			
Correction, Per Cent of Ml. Thiosulfate				Correction, Per Cent of Ml. Thiosulfate			
0	100.0	100.0	100.0	0	100.0	100.0	100.0
5	79.7	72.5	63.0	5	75.3	60.4	41.3
10	61.5	47.0	34.2	10	56.5	39.0	24.1
15	46.5	31.1	20.5	15	41.2	25.0	13.7
20	34.5	20.8	11.0	20	28.6	17.8	8.8
25	25.8	14.4	6.0	25	20.4	12.0	5.9
30	19.6	10.3	3.4	30	13.8	8.3	3.5
35	15.4	7.9	2.3	35	9.2	5.2	2.4
40	12.9	6.9	2.2	40	6.5	3.2	1.6
45	11.2	6.3	2.0	45	5.0	2.4	1.5
50	9.8	5.7	1.9	50	4.5	2.2	1.4
55	8.8	5.1	1.7	55	4.1	2.1	1.3
60	7.8	4.6	1.6	60	3.7	1.9	1.2
65	6.8	4.0	1.4	65	3.3	1.8	1.1
70	5.7	3.5	1.3	70	2.9	1.6	1.0
75	4.7	3.1	1.1	75	2.5	1.5	0.9
80	3.7	2.4	1.0	80	2.1	1.3	0.8
Lactose Hydrate and Dextrose				Lactose Hydrate and Levulose			
200 mg. lactose	100 mg. lactose	50 mg. lactose		200 mg. lactose	100 mg. lactose	50 mg. lactose	
0	100.0	100.0	100.0	0	100.0	100.0	100.0
5	71.5	62.6	54.5	5	60.7	34.4	19.0
10	47.3	30.5	22.6	10	39.8	19.3	11.7
15	29.5	16.0	9.7	15	26.4	11.2	6.6
20	19.0	7.6	3.4	20	15.8	6.6	2.1
25	13.4	4.3	1.5	25	10.3	3.8	1.0
30	9.4	2.8	1.4	30	5.6	2.0	0.9
35	7.2	2.5	1.3	35	2.4	0.9	0.8
40	6.4	2.4	1.2	40	1.0	0.8	0.8
45	6.1	2.2	1.1	45	0.9	0.8	0.7
50	5.7	2.1	1.1	50	0.8	0.7	0.6
55	5.4	1.9	1.0	55	0.7	0.6	0.5
60	5.0	1.7	0.9	60	0.6	0.5	0.5
65	4.7	1.5	0.8	65	0.6	0.4	0.4
70	4.4	1.4	0.7	70	0.5	0.4	0.3
75	4.0	1.2	0.6	75	0.4	0.3	0.2
80	3.7	1.0	0.5	80	0.3	0.2	0.1

The difficulties encountered in the preparation of pure maltose are well known. This sugar is generally made from starch by enzymatic degradation, and it must be separated from dextrose on the one hand and from higher saccharides on the other. There are no methods by which traces of these impurities may be determined. The writers have depended in their work on repeated crystallization of maltose and its effect on the reducing power toward the Steinhoff copper acetate reagent, and also on comparisons with reputedly pure samples of maltose obtained from various investigators. It was not found possible to prepare maltose with a reducing power less than that corresponding to 5 ml. of 0.1 N thiosulfate for 200 mg. of maltose. The reducing power of the same quantity of pure lactose was about one-half of that. Since lactose crystallizes much more readily than maltose, and yet exhibits reducing action toward the copper acetate reagent,



it appears probable that the reducing effect of maltose is not caused by impurities.

The reducing effect of maltose on the Steinhoff copper acetate reagent has been confirmed by Shapiro and Proferanzova (13). Tauber and Kleiner (15) have also observed that their modified Barfoed reagent is reduced by 2 mg. of maltose or 3 mg. of lactose.

Efforts have been made to discover a reagent which would be reduced by dextrose or levulose, but not by the authors' maltose or lactose. It was found that, if the Steinhoff reagent is diluted with water, or 0.5 gram of sodium salicylate is added to it, the reducing effect of the maltose or lactose becomes negligible, but the reducing effect of the modified reagent on dextrose is also lowered to such an extent that no practical advantage is gained. Even if later investigations should show that maltose or lactose, purified by more efficient methods, have no reducing effect on the Steinhoff reagent, they are nevertheless apt to affect the reducing power of dextrose or levulose in mixtures, as has been pointed out in the discussion of the reducing power of sugar mixtures. It would still be necessary to apply corrections for the maltose and lactose present, although the corrections would be different from those given in this paper.

The amount of the corrections to be applied, assuming the maltose and lactose to be pure, was evaluated by adding 50, 100, and 200 mg. of maltose hydrate, of lactose hydrate, and of equal parts of these sugars to varying quantities of dextrose, levulose, and invert sugar, respectively, and determining the reducing power of the mixtures on the copper acetate reagent. All the data were plotted and the figures given in Table IV were taken from the curves, for mixtures of maltose and dextrose, lactose and dextrose, maltose and levulose, and lactose and levulose. The tables show directly the per cent of the milliliters of 0.1 *N* thiosulfate to be deducted from those actually obtained, for 200, 100, and 50 mg. of either maltose or lactose in the presence of up to 80 mg. of either dextrose or levulose. The values for intermediate quantities of maltose or lactose and for intermediate quantities of dextrose and levulose are found by interpolation. This cross interpolation can be made more quickly by means of the curves, but the actual figures instead of the curves are reproduced in this paper, because the curves have to be drawn on a rather large scale to be useful.

The corrections to be applied for mixtures of maltose and lactose in the presence of mixtures of dextrose and levulose were found to accord with the fractional proportionality rule: The correction for maltose plus lactose is proportional to the partial concentration of either sugar, but on the basis of the total concentration of maltose plus lactose. Similarly, the correction to be applied for the effect of maltose or lactose on a mixture of dextrose and levulose is based on the total concentration of the last two sugars, and their proportion in the mixture. The use of the correction tables is explained in greater detail in the following example.

### Method of Calculation

The results of the analyses are calculated by a series of approximations which are continued until two successive calculations give practically identical results.

A solution was prepared, containing in each 100 ml., 30 mg. of dextrose, 200 mg. levulose, 690 mg. maltose hydrate, and 90 mg. lactose hydrate.

In this first check analysis the mucic acid method was used for the determination of the lactose, 100-ml. portions of the solution being taken. This gave an average of 14.6 mg. of mucic acid, corresponding, according to van der Haar's table, to 38.75 mg. of galactose, which multiplied by 2.2 is equivalent to 85.2 mg. of lactose in 100 ml., or 8.5 mg. in 10 ml.

Ten milliliters of solution gave 0.0728 gram of copper with the Jackson and Mathews reagent; this corresponds to 23.3 mg. of apparent levulose ( $R_1$ ).

Ten milliliters of solution gave a titration value of 11.6 ml. of 0.1 *N* thiosulfate with the Steinhoff copper acetate reagent, equivalent to 25.0 mg. of levulose ( $R_2$ ); and of 20.4 ml. of thiosulfate with the Steinhoff copper tartrate reagent, equivalent to 64.8 mg. of dextrose ( $R_3$ ).

Hence,

$$L = 8.5 \text{ mg.}$$

$$R_1 = 23.3 \text{ mg.}$$

$$R_2 = 25.0 \text{ mg.; } a = 0.819$$

$$R_3 = 64.8 \text{ mg.; } b = 0.896, c = 0.532, d = 0.666$$

First approximation:

$$G = \frac{25.0 - 23.3}{0.819 - 0.081} = 2.3 \text{ mg.}$$

$$F = 25.0 - (2.3 \times 0.819) = 23.1 \text{ mg.}$$

Percentage ratio of  $G$  to  $F$  is as 9 to 91;  $a = 0.813$

$$G = \frac{25.0 - 23.3}{0.813 - 0.081} = 2.3 \text{ mg.}$$

$$F = 25.0 - (2.3 \times 0.813) = 23.1 \text{ mg.}$$

$$M = \frac{64.8 - [2.3 + (23.1 \times 0.896) + (8.5 \times 0.666)]}{0.532} = 67.9$$

Result of first approximation, for 10 ml. of solution:

$$G = 2.3 \text{ mg.}$$

$$F = 23.1 \text{ mg.}$$

$$M = 67.9 \text{ mg.}$$

$$L = 8.5 \text{ mg.}$$

Second approximation, correction to  $R_1$ :

$$67.9 \text{ mg. } M \text{ equivalent to } 67.9:26 = 2.61 \text{ mg. } F$$

$$8.5 \text{ mg. } L \text{ equivalent to } 8.5:25.6 = 0.33 \text{ mg. } F$$

$$\text{Total correction} = 2.94 \text{ mg. } F$$

$$\text{Corrected } R_1 = 23.3 - 2.9 = 20.4 \text{ mg.}$$

Correction to  $R_2$ :

$$\text{Total dextrose plus levulose} = 25.4 \text{ mg.}$$

$$\text{Total maltose plus lactose} = 76.4 \text{ mg.}$$

	Correction (Table IV)
	%
25 $F$ + 76 $M$	9
25 $F$ + 76 $L$	2.5
25 $G$ + 76 $M$	10
25 $G$ + 76 $L$	2.5
25 $F$ + 68 $M$ gives 9 $\times$ 68:76	8.05
25 $F$ + 8 $L$ gives 2.5 $\times$ 9:76	0.30
25 $F$ + 68 $M$ + 9 $L$	8.35
25 $G$ + 68 $M$ gives 10 $\times$ 68:76	8.95
25 $G$ + 8 $L$ gives 2.5 $\times$ 9:76	0.30
25 $G$ + 78 $M$ + 9 $L$	9.25
23 $F$ + 68 $M$ + 9 $L$ gives 8.35 $\times$ 23:25	7.68
2 $G$ + 68 $M$ + 9 $L$ gives 9.25 $\times$ 2:25	0.74
23 $F$ + 2 $G$ + 68 $M$ + 9 $L$	8.42

Corrected thiosulfate titer, Steinhoff acetate reagent, is 11.6 - (11.6  $\times$  0.0842) = 10.6 ml.

Equivalent corrected  $R_2 = 23.2$ ;  $a = 0.844$

$$G = \frac{23.2 - 20.4}{0.844 - 0.081} = 3.7 \text{ mg.}$$

$$F = 23.2 - (3.7 \times 0.844) = 20.1 \text{ mg.}$$

Percentage ratio of  $G$  to  $F$  is as 15.5 to 84.5;  $a = 0.835$

$$G = \frac{23.2 - 20.4}{0.835 - 0.081} = 3.7 \text{ mg.}$$

$$F = 23.2 - (3.7 \times 0.835) = 20.1 \text{ mg.}$$

$$M = \frac{64.8 - [3.7 + (20.1 \times 0.896) + (8.5 \times 0.666)]}{0.532} = 70.3 \text{ mg.}$$

Result of second approximation, in 10 ml. of solution:

$$G = 3.7 \text{ mg.}$$

$$F = 20.1 \text{ mg.}$$

$$M = 70.3 \text{ mg.}$$

$$L = 8.5 \text{ mg.}$$

Third approximation, correction to  $R_1$ :

$$70.3 \text{ mg. } M \text{ equivalent to } 70.3:26 = 2.70 \text{ mg. } F$$

$$8.5 \text{ mg. } L \text{ equivalent to } 8.5:25.6 = 0.33 \text{ mg. } F$$

$$\text{Total correction} = 3.03 \text{ mg. } F$$

$$\text{Corrected } R_1 = 23.3 - 3.0 = 20.3 \text{ mg.}$$

Correction to  $R_2$ :

$$\text{Total dextrose plus levulose} = 23.8 \text{ mg.}$$

$$\text{Total maltose plus lactose} = 78.8 \text{ mg.}$$



	Correction %
24 F + 79 M	10.5
24 F + 79 L	3.5
24 G + 79 M	12.0
24 G + 79 L	3.5
24 F + 70 M gives $10.5 \times 70:79$	9.3
24 F + 9 L gives $3.5 \times 9:79$	0.4
24 F + 70 M + 9 L	9.7
24 G + 70 M gives $12.0 \times 70:79$	10.6
24 G + 9 L gives $3.5 \times 9:79$	0.4
24 G + 70 M + 9 L	11.0
20 F + 70 M + 9 L gives $9.7 \times 20:24$	8.1
4 G + 70 M + 9 L gives $11.0 \times 4:24$	1.8
20 F + 4 G + 70 M + 9 L	9.9

The corrected thiosulfate titer, Steinhoff acetate reagent, is  $11.6 - (11.6 \times 0.099) = 10.45$  ml.

Equivalent corrected  $R_2 = 22.9$ ;  $a = 0.848$

$$G = \frac{22.9 - 20.3}{0.848 - 0.081} = 3.4 \text{ mg.}$$

$$F = 22.9 - (3.4 \times 0.848) = 20.0 \text{ mg.}$$

Percentage ratio of  $G$  to  $F$  is as 14.5 to 85.5;  $a = 0.839$

$$G = \frac{22.9 - 20.3}{0.839 - 0.081} = 3.4 \text{ mg.}$$

$$F = 22.9 - (3.4 \times 0.839) = 20.0 \text{ mg.}$$

$$M = \frac{64.8 - [3.4 + (20.0 \times 0.896) + (8.5 \times 0.666)]}{0.532} = 71.1 \text{ mg.}$$

Result of third approximation:

$$G = 3.4 \text{ mg.}$$

$$F = 20.0 \text{ mg.}$$

$$M = 71.1 \text{ mg.}$$

$$L = 8.5 \text{ mg.}$$

These values agree so closely with those obtained in the second approximation that further calculation is unnecessary. The final results are therefore:

	Taken Mg.	Found Mg.
Dextrose	3.0	3.4
Levulose	20.0	20.0
Maltose hydrate	69.0	71.1
Lactose hydrate	9.0	8.5

Four other check analyses, in which the lactose was determined by the fermentation method, gave these results:

	2		3		4		5	
	Taken Mg.	Found Mg.	Taken Mg.	Found Mg.	Taken Mg.	Found Mg.	Taken Mg.	Found Mg.
Dextrose	20.0	20.5	2.3	2.1	0.0	0.9	26.4	27.5
Levulose	5.0	4.8	16.5	17.5	17.6	17.5	5.4	5.6
Maltose hydrate	20.0	17.5	28.5	26.4	35.0	38.7	20.7	16.4
Lactose hydrate	30.0	29.6	19.5	19.5	22.4	22.4	35.5	35.5

The quantities of dextrose, levulose, and lactose found check well with those taken, but the maltose figures show larger discrepancies because this sugar is determined by difference, and the errors in all four determinations accumulate in this one result. In two of the mixtures the maltose was found too high, in the others too low. The percentage error is generally smaller when the quantity of maltose is high than when it is low.

The principal criterion for the accuracy of the maltose determination is the amount of the total sugars obtained with Fehling solution. The milliliters of thiosulfate found upon eight different mixtures of the four sugars compared as follows with those calculated by Formula 4:

	Found Ml.	Calculated Ml.
1	20.39	20.08
2	22.35	22.68
3	21.31	21.42
4	17.20	17.58
5	16.63	16.97
6	14.44	14.67
7	16.76	16.23
8	20.40	20.71

The differences range from +0.53 to -0.31 ml. of thiosulfate, corresponding to about 2 to 3 mg. of maltose hydrate. They are in most cases somewhat larger than the experimental error of 0.1 to 0.2 ml. of thiosulfate, but the positive and negative errors nearly balance each other. It is probable that the variation in the proportions of the individual sugars in the mixtures affects the reducing ratio of each sugar, as previously explained. The best check on the accuracy of the analysis of an unknown sample is to prepare a mixture of the sugars in the proportions found, to analyze it, and to compare the results with those obtained in the analysis of the sample.

The errors in the results of the check analyses reported above are not any larger than may be expected in the analysis of mixtures of four sugars by indirect methods, as has been pointed out by Browne (2). The limitations of such methods must always be kept in mind in the interpretation of the results obtained upon an unknown sample.

The accuracy of the results, especially in the determination of maltose, would be increased if at least one more sugar could be determined directly. Or the sum of two or three of the sugars might be ascertained by an independent method, as a check on the results. These possibilities will be investigated.

## Summary

Previous studies on the determination of dextrose and levulose have been extended to mixtures also containing maltose and lactose. In the proposed method the total reducing sugars are determined by means of Fehling solution, the monosaccharides with Steinhoff's modification of Barfoed's reagent, and levulose by the method of Jackson and Mathews. Lactose is found by oxidation to mucic acid, or preferably by copper reduction after fermenting off the other sugars. Four equations are thus obtained from which the percentage of each sugar can be calculated. It has been found that both maltose and lactose have a slight reducing effect on Steinhoff's reagent as well as on Jackson and Mathews' reagent, and it is necessary to apply corresponding corrections. The quantities of dextrose, levulose, and lactose found in known mixtures agree well with those taken, but the result for the maltose is less reliable because it is obtained by difference.

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# Liquid-Liquid Extraction in the Separation of Petroleum Acids

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WHILE recent developments in the petroleum industry have made liquid-liquid extraction theory, uses, and apparatus well known in that industry, the organic chemist generally still contents himself with simple separatory funnel extraction or with the use of apparatus of the Soxhlet type. This is due, no doubt, in part to the fact that no efficient laboratory-size extraction apparatus has become generally known.

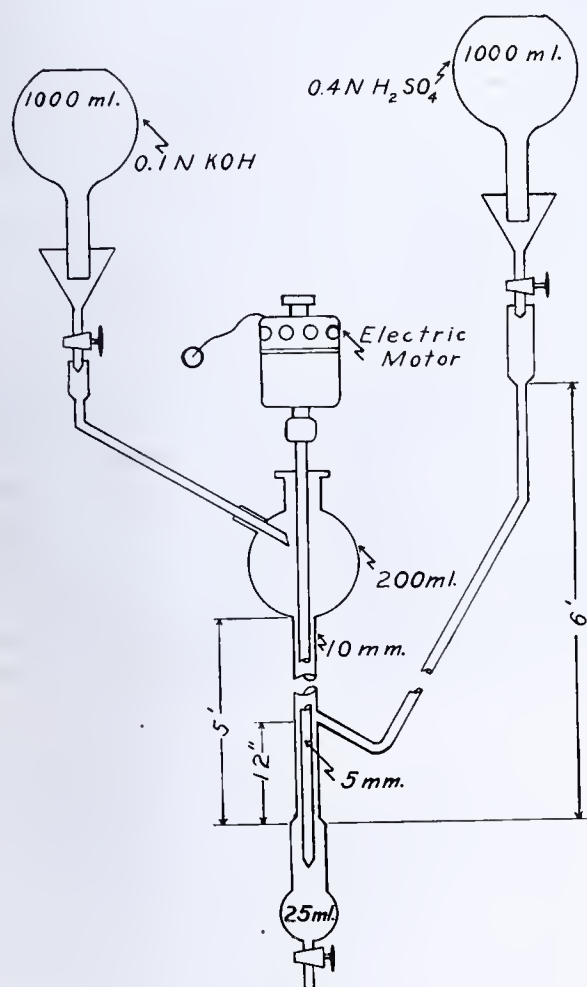


FIGURE 1

Jantzen and co-workers (2) in the course of a thorough study of the use of liquid-liquid extraction in the separation of coal-tar bases (3, 5) developed and tested an efficient apparatus but did not describe it in detail and their work appears to have escaped general attention. Evans and co-workers (1) in 1934 described a rotary column that proved very effective in the isolation of vitamins. Numerous packed columns have been developed in petroleum laboratories, but most of them require several liters of solution. For use with such volumes the packed column appears to be the most convenient extractor.

The 14-meter columns of Mair and Schickanz (4) are simple in operation and may, of course, be modified for use (made as short as 60 cm.) in an ordinary laboratory, provided circulation is continued for a longer period of time, but the authors know of no way of using simple solvent extraction in the separation of petroleum acids. They have, however,

used a Mair and Schickanz heavy-solvent type of apparatus, modified to use a rotary column, for some months in the extraction of esters of petroleum acids with water as solvent.

Rotary columns of the type developed by Jantzen differ from packed and unpacked columns only in the extraction column itself, the upper and lower sections and accessories being varied to meet conditions.

While a number of types of apparatus and schemes have been tried in this work, only two modifications will be described.

Figure 1 shows column 1 designed like Jantzen's as far as his description permits.

Between the usual upper and lower separating sections is the column proper, consisting merely of a glass tube within which a smaller closed tube or rod is rotated at 200 to 500 r. p. m. The exact size of rotator, speed of rotation, and concentration of solutions used in the separation of complex mixtures of acids depend mainly on the emulsifying tendency of the mixture. If the apparatus is operated so as to remove the hydrocarbons and weakest acids first from a mixture of petroleum acids, the column tends to "slug" or cease countercurrent circulation unless the solutions are as dilute as 0.1 *M* and the rotator is operated at a relatively low speed, but after the first cut or two have been removed this tendency causes little or no trouble.

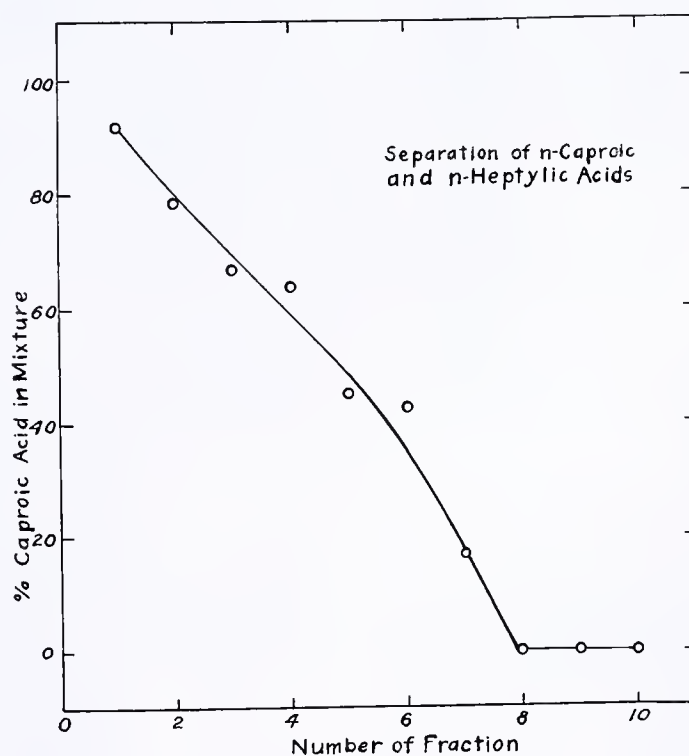


FIGURE 2

In the separation of *n*-hexoic from *n*-heptoic acid selected as a test mixture, 15.3 grams of the former and 16.4 grams of the latter were added to the column, which was then filled with petroleum ether to a point just below the upper section. Tenth molar potassium hydroxide was added at the top at a rate of about two drops a second, while 0.4 *N* sulfuric acid was added at the connection near the bottom at a rate ensuring a slight excess of acid as indicated by methyl orange. The interface was held near the bottom of the rotor. The droplets of potassium salt solution descended in very flat spirals through the petroleum ether-filled column until they reached the sulfuric acid inlet where both of the weak acids were liberated. A



small portion of the acids, mostly hexoic at first, dissolved in the descending acid water spiral while most of the weak acids accumulated and diffused upward where interchange with descending potassium salts took place, hexoic acid replacing heptoic until equilibrium was established. In the run on which the data of Figure 2 are based the column was run until 1 liter of 0.1 *M* potassium hydroxide had passed through the column, and the accumulated acids of the water layer were extracted with petroleum ether and added to the top of the column. The next liter of water layer collected was extracted for cut 1, the next for cut 2, etc. The per cent of each acid present in each carefully treated cut was calculated from the neutralization equivalent.

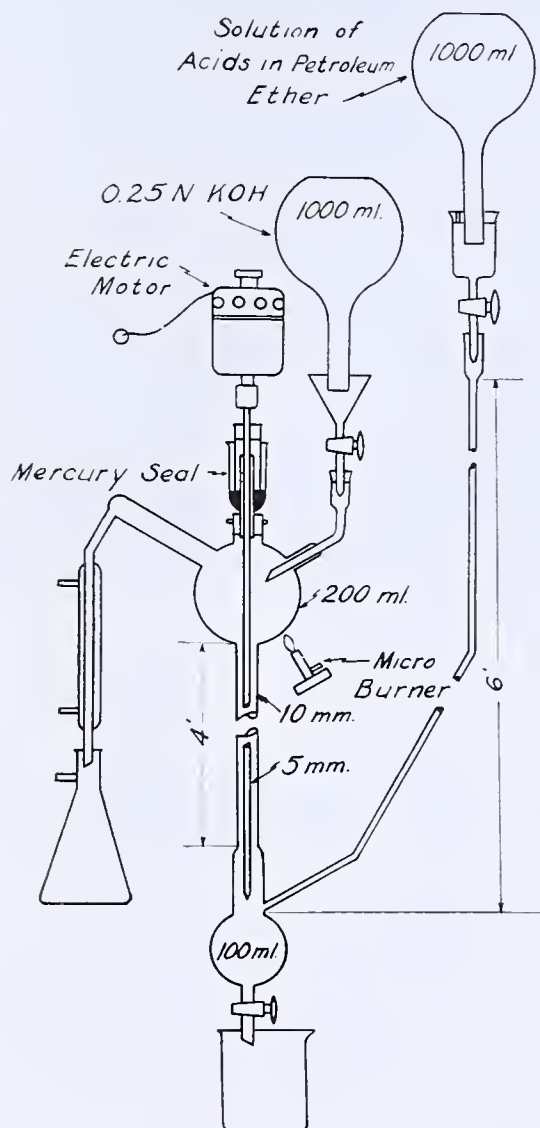


FIGURE 3

Figure 3 shows column 2, also designed for batch extraction, but one in which the weaker or less soluble acids were to be obtained as first cuts instead of the strong ones as in column 1.

The acids and alkali again pass each other in a very flat spiral but in this case a 0.25 *N* solution of potassium hydroxide was continuously added at the top while a 0.1 *N* Skelly Solve solution of one of three consecutive very closely related distillation fractions of petroleum acids from light burner oil wash, obtained in the refining of Texas petroleum (furnished through the courtesy of the Humble Oil and Refining Company at its Baytown Refinery), was added at the bottom at such a rate that about 80 per cent of the acids were neutralized by the potassium hydroxide coming down. As the solution of weak acids arrived at the top the petroleum ether was distilled off,

thus forcing the alkali to pass first through a concentrated solution of the weakest acids. After all the acids had been added in this way the column was rinsed with 100 cc. of pure solvent. The column was then emptied and the 20 per cent cut of weakest acids isolated. The stronger acids were then liberated with sulfuric acid, again taken up in petroleum ether, and passed through the column again and again until the desired number of cuts had been obtained.

Cuts 5, 6, and 7 of Figure 4 were obtained after repeated fractionation of the Texas acids through a 180-cm. (6-foot) efficient fractionating column. Density and refractive index were changing only slightly from cut to cut and series to series, so that little more separation would have been obtainable with any reasonable amount of refractionation. After each of the fractions had been cut into five extraction cuts by column 2 they had the density and index of refraction shown for the three series of extracted acids of Figure 4.

Since Figure 4 indicates that each of the three sets of five cuts shows analogous changes in constants, additional tests were run by combining cuts 1, 2, 1', and 1"; 3, 2', 3', and 2"; 4, 4', 3", and 4"; and 5, 5', and 5" and reextracting each combined lot in the same manner. The last cut of each run was combined with the next. These steps were then repeated another time for some and twice more for others to yield the EIII and EIV fractions of Figure 5.

Figure 5 shows again the constants of the original distillation cuts along with the final values. The remarkable change in range of constants of a series of acids that were changing only very gradually on redistillation is brought out clearly.

No rotary column so far tested in this laboratory has a throughput of more than 250 ml. of each solution per hour, so that extraction of large volumes by such columns would be tedious. It is hoped that columns now being built will overcome this defect. At present large volumes are being extracted in 5 to 6 stages without reflux with a modified separatory funnel scheme following a scheme like the one presented by Morton (5, p. 200).

The isolation and characterization of individual acids are now under way and will be reported in a future paper, but the great advantage of fractional distribution, based as it is

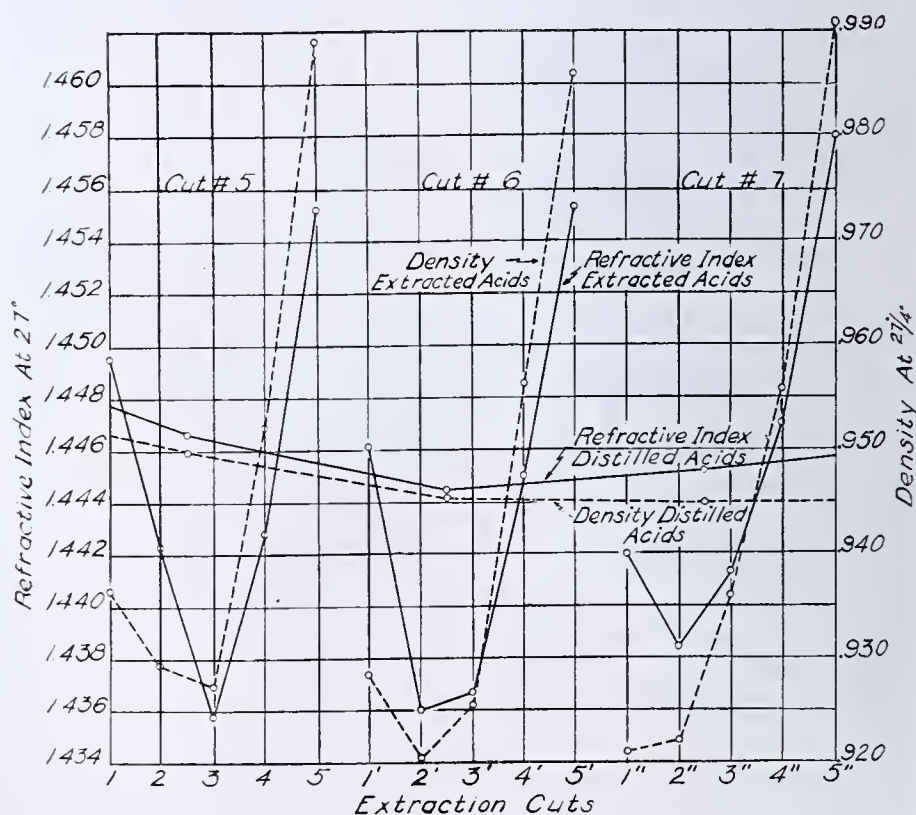


FIGURE 4



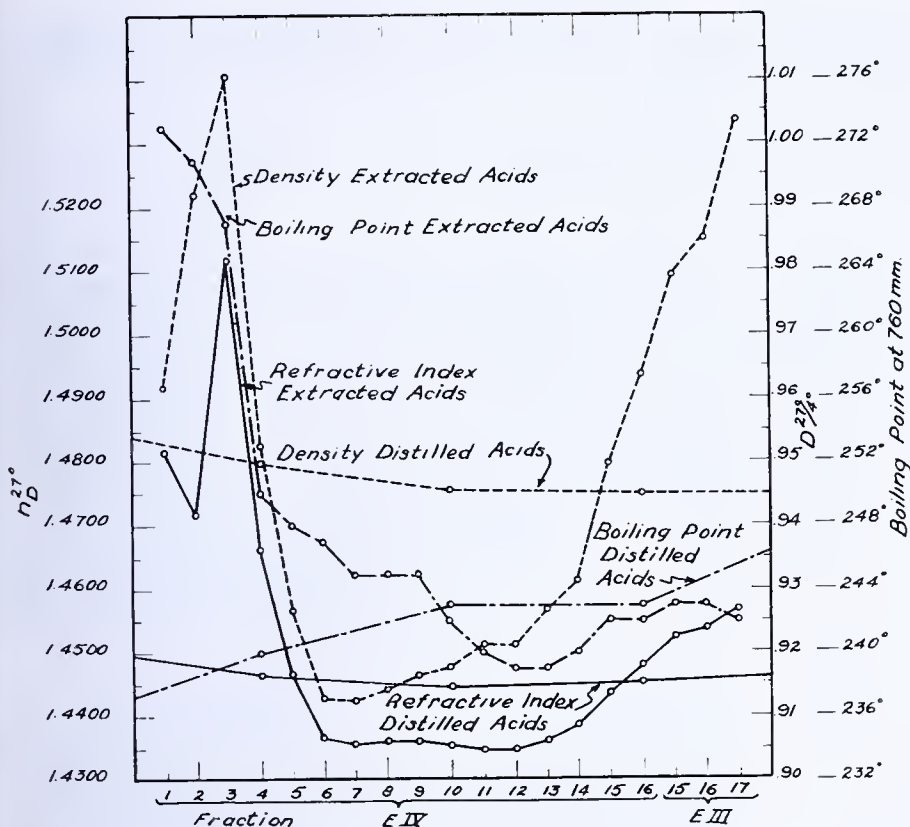


FIGURE 5

on differences in  $K_a$  values and in structure as a supplementary method to fractional distillation, is apparent.

**Summary**

The advantages of fractional extraction following fractionation by distillation in the separation of very complex mixtures of closely related compounds like those found in petroleum acids are stressed.

Two rotary columns for countercurrent extraction with or without reflux are described.

Results obtained in the separation of caproic and *n*-heptylic acids and of a complex petroleum acid mixture are presented.

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## Preparation of Hydriodic Acid Suitable for Alkoxyl and Friedrich-Kjeldahl Nitrogen Determinations

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COMMERCIALY available hydriodic acid has been used in the many volumetric methoxyl determinations made in this laboratory during the past few years (1). These acids invariably gave high blank values, which were materially reduced by a special purification procedure. However, instead of purifying a commercial acid, it has been found more economical and as convenient to prepare an acid for the purpose. The product obtained by the procedure given below is satisfactory, as it is almost, if not entirely, free from blank and is stable for a long time.

The same considerations also apply to hydriodic acid used in the Friedrich-Kjeldahl nitrogen determinations (2), in that the blanks on the specially prepared acids have been found to be from four to eight times lower than those of any commercial acids employed.

The preparation of the acid for the purposes under discussion involves the well-known reduction of iodine with hypophosphorous acid and the scrubbing of the resulting constant-boiling liquid with carbon dioxide.

For this purpose 254 grams of iodine and 185 grams of water were heated to about 50° C. in a 500-cc. flask with a ground-joint condenser, and 66 grams of 50 per cent hypophosphorous acid were added portionwise at such a rate that the mixture boiled continuously until the iodine was reduced. Heat was then applied to the flask and the boiling was continued for 3 hours, during which time a stream of carbon dioxide was passed through the

solution. The position of the reflux condenser was then changed to allow distillation, and the constant-boiling hydriodic acid was collected. The yield was 447 grams. The preparation was stored in dark bottles and preserved by the addition of a little 50 per cent solution of hypophosphorous acid (about 1 cc. per pound).

A preparation made from one lot of "pure chemicals" of a reputable brand gave a zero alkoxyl blank and a blank of 0.02 cc. of 0.01 *N* acid for the Friedrich-Kjeldahl nitrogen method. Another preparation made from a different lot of similar chemicals gave an alkoxyl blank of 0.01 cc. of 0.05 *N* thiosulfate.

Hydriodic acid prepared in this manner from commercial hypophosphorous acid or hypophosphites cannot be used in the Zeisel method, as apparently they all contain sulfates. These are reduced with the formation of hydrogen sulfide, which naturally interferes by forming silver sulfide. If, however, sulfur-free hypophosphorous acid or hypophosphites were prepared for the purpose, the product would be satisfactory.

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# Determining the Sediment Content of Fuel Oil

## A New Method

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MUCH of the heavy, viscous so-called "bunker" fuel oil of the present day contains residual products from cracking operations. This material varies widely in character with the nature of the crude oil from which it is derived and the method and degree of cracking to which it has been submitted.

Cracked residues are not always completely soluble in petroleum distillates or uncracked residues, thus complicating the problem of preparing merchantable blends. They usually contain solid or semisolid particles which are not objectionable if dispersed, but which sometimes agglomerate in the form of troublesome sludges or deposits if the fuels are subjected to unfavorable conditions of storage and use.

The solubility problem at one time was most serious, when it was frequently necessary to blend cracked residues with paraffinic gas oils. Difficulties of this particular kind are less frequent today, since the oil industry is plentifully supplied with cracked distillates for blending purposes. However, the solubility problem in lesser degrees still exists, even though it may not be recognized as such. The problem of minimizing the precipitation of residues and sludges is still frequently troublesome, and even the best informed technologists are not always able to predict whether or not a given oil will cause difficulty.

Practically all residual fuel oils deposit sediment and sludge in storage tanks (usually an emulsion of water, oil, and insoluble material). The rate at which these deposits accumulate is controlled in part by the character of the oil, and there is a definite need for a laboratory test method capable of evaluating this detail of practical quality. Storage tanks must, of course, be cleaned periodically, but it is commercially advantageous to perform this operation as infrequently as possible. Furthermore, accumulated sediments may cause serious difficulties by becoming dislodged and being carried into the burner, thus interfering with satisfactory operation.

The actual use of bunker fuel oils generally involves either one or two heating operations. It is sometimes necessary to warm the contents of storage tanks in order to facilitate pumping to boiler rooms, and it is practically always necessary to pass the fuel through a heat exchanger (preheater), which reduces its viscosity so as to ensure proper atomization by the burner. The surfaces of these preheaters are prone to become fouled with deposits of insoluble material formed in or separated from the fuel at the elevated temperatures to which it has been subjected. Such fouling is known to vary in intensity with different oils, and a laboratory test is also needed to evaluate this tendency.

### Present Laboratory Test Methods

The "sediment by extraction" test (2) is commonly applied to bunker fuel oil and apparently affords some degree of protection against excessive deposition of sludge in storage, although it does not always rate oils correctly with respect to this tendency. It seems to be valueless in predicting a

A practical method has been developed for determining the sediment content of residual fuel oil without the use of a diluent which may dissolve or disperse nonfilterable material. The method is useful in predicting the storage performance of fuel oils and gives promise of value in connection with tests for determining tendency toward fouling of preheaters.

fuel's stability in contact with preheater surfaces. As a matter of fact, at present there is no generally accepted laboratory method which seems to correlate with known cases of preheater clogging. Various tests have been proposed and the problem is being studied intensively in several laboratories (1,3), including those with which the writers are associated.

### New Developments

The present report describes a new method for determining sediment which avoids certain theoretically objectionable features of the sediment by extraction test and which has, up to date, been found to correlate accurately with the actual tendency of fuel oils to settle. The new method has also given promise as a tool for use in conducting tests for predicting the tendency of fuels to clog preheaters. It can be carried out in a shorter elapsed time than the sediment by extraction test.

The new method involves filtering undiluted but heated oil through an asbestos mat in a special steam-jacketed filter funnel, washing the residue free of oil with a high-flash-point paraffinic naphtha ("Stoddard solvent"), drying, and weighing. It avoids the abnormalities incident to the use of an

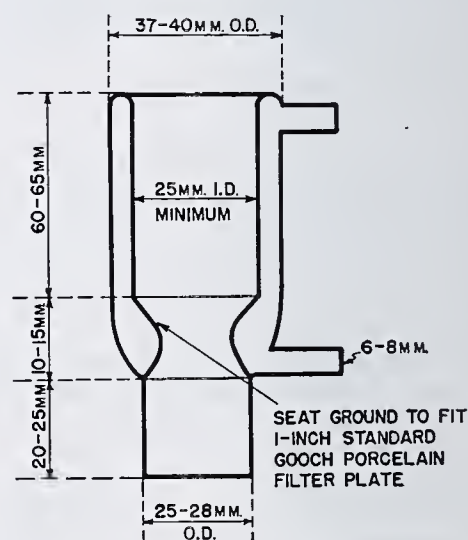


FIGURE 1. STEAM-JACKETED SUCTION FILTER FUNNEL

aromatic solvent such as the benzene employed in the sediment by extraction test. The sediment contained in cracked residues consists in part of aggregates of small primary particles held together by an asphaltic binder. The benzene solvent used in the sediment by extraction test is capable of dissolving the binder and dispersing aggregates which exist in the actual oil and which are capable of settling out as sludge, or in extreme cases of clogging strainers. Cracked fuel oil may also contain solid asphaltic material which is soluble in benzene but insoluble in the oil. The new sediment



test simulates actual service conditions which involve heating the fuel but not thinning it with an aromatic solvent.

Apparatus and Reagents

ASBESTOS. Medium-fiber, acid-washed asbestos suspended in distilled water with a concentration of 6 grams per liter.

WASH NAPHTHAS. A high-boiling petroleum naphtha having an initial boiling point of 149° C. (300° F.), or higher, and a final boiling point not exceeding 213° C. (415° F.). The aniline point should be between 40° and 60° C. A commercial product sold as "Stoddard solvent" usually meets these requirements.

A. S. T. M. precipitation naphtha.

FILTER FUNNEL. A steam-jacketed suction filter funnel of glass as shown in Figure 1, with a 2.5-cm. (1-inch) perforated porcelain filter plate, ground in to fit. (This device is available from the firm of Gottlieb Greiner, 50 Dey St., New York, N. Y.)

ACCESSORIES. Suction flask adapter, rubber hose, pump, steam supply, etc. The pump should be capable of holding an absolute pressure of 254 mm. (10 inches) in the suction flask while liquid is on the filter.

Procedure

PREPARATION OF FILTER. The asbestos suspension is shaken thoroughly and a 50-ml. portion withdrawn, which contains approximately 0.3 gram of asbestos. Without applying suction, the funnel is filled with the suspension and allowed to stand 15 to 20 seconds, after which light suction is applied. When the liquid from this first portion of the suspension has passed through the plate, a thin pad of asbestos, having no holes, will be formed on the perforated plate. Full suction is then applied and the balance of the 50-ml. of asbestos suspension poured into the funnel. After the liquid has been filtered through, the asbestos mat is washed with 50 ml. of distilled water and finally with 10 to 15 ml. of acetone or alcohol. The funnel is then dried in an oven at 120° C. (248° F.) for an hour and cooled in a desiccator before weighing.

PREPARATION OF SAMPLE. Sample containers are warmed until their entire contents have come to a temperature of 49° to 52° C. (120° to 125° F.). The fuel oil in the sample container is thoroughly mixed, preferably with a suitable stirrer operated by hand or by power.

FILTRATION OF FUEL OIL. An adequate quantity of the warmed and mixed sample is withdrawn from the container and allowed to cool approximately to room temperature. Twenty grams are weighed with an accuracy of ±0.1 gram directly into the tared filter funnel prepared as described above.

The filter funnel containing the sample is attached to the suction flask and the top side arm connected to the steam supply, the bottom outlet going to the waste. The current of steam is started and suction applied at first gently, then to the full capacity of the pump. Vacua higher than 508 mm. (20 inches) of mercury or 254 mm. (10 inches) of mercury absolute pressure on the suction side must be avoided, because of possible rupture of the asbestos filter pad. The oil will usually filter through in from 5 to 10 minutes, although certain samples may take longer.

After all the oil has filtered through the funnel, as evidenced by dryness of the mat and cessation of oil drops falling into the suction flask, the accumulated sediment on the side walls of the funnel is washed down with the high-boiling naphtha and the precipitate on the filter pad is carefully washed. A total of 90 ml. of naphtha is used.

Finally, 10 ml. of A. S. T. M. precipitation naphtha are poured over the precipitate and filtered through.

The annular steam jacket is dried, first by blowing out condensed water with air, then by running in a little acetone or alcohol, and subsequently blowing approximately dry with air. The funnel is then dried in an oven at 120° C. (248° F.) for an hour and cooled in a desiccator before weighing. The sediment is reported on a weight per cent basis and is quoted as sediment number.

Accuracy of Hot Filtration Test

The reproducibility of the method is illustrated by the figures in Table I which show the results obtained by several laboratories on the same two samples. Generally speaking, it appears that a single operator may expect a maximum deviation of 0.02 sediment number between checks, and that different operators in different laboratories may be ex-

TABLE I. REPRODUCIBILITY OF RESULTS OF HOT FILTRATION SEDIMENT METHOD

Laboratory	Sample 1569 <sup>a</sup>		Sample 1570 <sup>b</sup>	
	Individual determinations (sediment number)	Laboratory average	Individual determinations (sediment number)	Laboratory average
A	0.20, 0.21, 0.23	0.213	0.16, 0.18, 0.16	0.166
B	.....	0.240	.....	0.180
C	0.17, 0.20	0.185	0.21, 0.24	0.225
D	0.19, 0.19	0.190	0.16, 0.17	0.165
E	0.195, 0.195, 0.204, 0.213	0.202	0.174, 0.176, 0.166, 0.173	0.172
F	0.218, 0.215	0.217	0.168, 0.165	0.167
G	0.196, 0.192, 0.203	0.197	0.188, 0.174, 0.170	0.177
H	0.209, 0.199, 0.197, 0.208	0.203	0.140, 0.132, 0.137, 0.136	0.136
I	0.208, 0.203	0.206	0.109, 0.128	0.118
J	0.19, 0.20	0.195	0.14, 0.15	0.145
K	0.217, 0.230, 0.224, 0.229	0.222	0.156, 0.148, 0.152, 0.167	0.157
	0.219, 0.215, 0.220, 0.222	0.206	0.150, 0.151, 0.162, 0.166	0.183
	Grand average		.....	
	Average deviation among laboratories	0.009	.....	0.026

<sup>a</sup> Specific gravity, 0.983. Gravity, 12.4° A. P. I. Viscosity, 70.1 seconds Furol at 122° F.  
<sup>b</sup> Specific gravity, 0.985. Gravity, 12.1° A. P. I. Viscosity, 71.6 seconds Furol at 122° F.

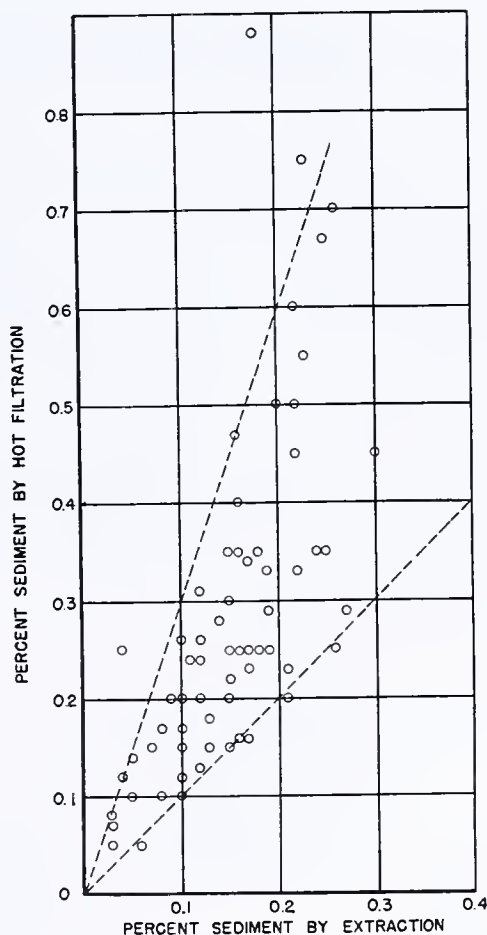


FIGURE 2. COMPARISON OF SEDIMENT BY EXTRACTION WITH SEDIMENT BY HOT FILTRATION

pected to check the grand average within ±0.025 sediment number.

The chief cause of deviations in laboratory results is probably failure to obtain representative test portions from the oil samples. Thorough stirring is an absolute essential and excessive heating or contact with air must be avoided.

Comparison of Results by Two Methods

The theoretical advantages of the hot filtration method over the extraction method have already been discussed. The former would be expected to yield higher results as it separates material which would be dissolved or dispersed by benzene. The figures represented graphically in Figure 2 demonstrate that such is the case and that the ratio between



sediment figures from the two methods is usually between 1 to 1, and 3 to 1. Figure 2 also indicates that the two methods do not rate oils in the same order.

### Practical Applications of Hot Filtration Method

The hot filtration method determines the content of material capable of settling when fuel oil is stored. It does not, of course, indicate the rate of settling and it involves a somewhat higher temperature than those normally existing in storage tanks. It has been developed primarily as a practical means of obviating the fundamental deficiencies of the benzene extraction method, and has already been put into routine operation for this purpose.

The authors believe that it possesses a much wider field of usefulness and are using it in their investigations of the problem of heater fouling. It is planned to report the results of this study in another paper.

### Acknowledgment

Acknowledgment is due to E. W. Dean of the Standard Inspection Laboratory, Standard Oil Development Company, for constructive criticism of the method and for assistance with the manuscript.

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## Plastometry of Synthetic Resins

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When testing the value of resins, especially of hardening synthetic resins, the two properties to be given most consideration are the hardness (weakening point) and the hardening velocity.

New apparatus to measure these properties, particularly the Schopper-Houwink plastometer, is described. Experimental results are discussed with their technical and scientific applications.

WHEN using resins for molding purposes, and also in many cases in varnishes and lacquers, the purely chemical testing methods (5) are of little use. The chief points to be investigated are their weakening point, their chemical reactivity, and the properties of the molded product. The weakening point is important, because generally the resins have to be melted in order to mix them with fillers and other substances. Mass production is possible only when a constant weakening point can be guaranteed. The weakening point for a certain resin is dependent on its degree of polymerization. The same holds for more physical properties: Hardness, viscosity, and yield value (if present) all increase on polymerizing. This means that, as a matter of principle, for control purposes one is free to determine any of these properties he likes to.

It has been proved to be practical to measure what may be called the plastometer hardness, this being (by definition) the height,  $h_{30}$  (12, 16, 17), of a resin specimen, originally 10 mm. in diameter and 5 mm. in height, after 30 minutes' compression by a 5-kg. weight at a fixed temperature between two parallel plates. Pure physical constants like viscosity coefficient and yield value can be derived from this conventional compression procedure. There are many reasons for preferring this hardness to such other constants as the weakening point according to Krämer-Sarnow, the ring and ball (2) melting point, and the penetration (1). In many cases the resins have such a high weakening point that the Krämer-

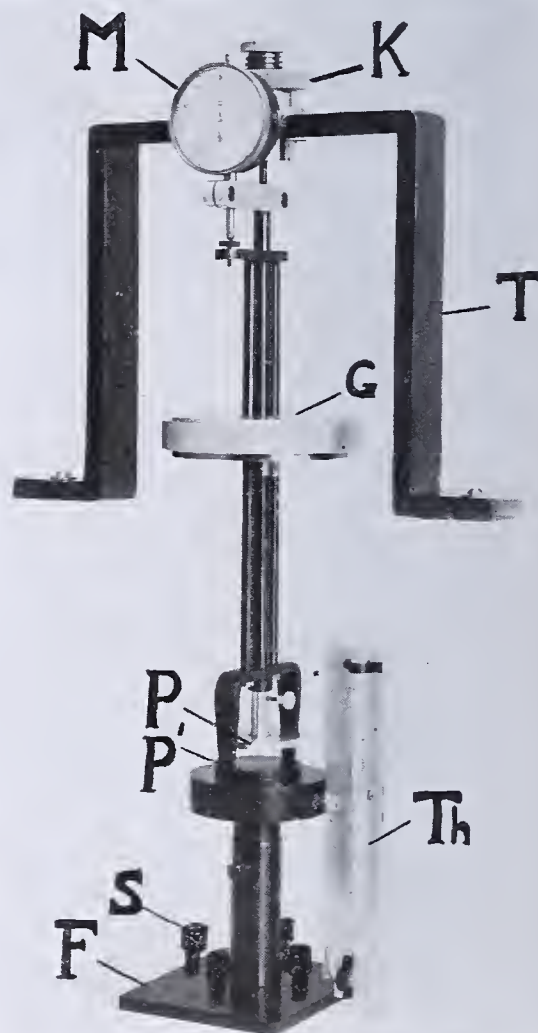


FIGURE 1. SCHOPPER-HOUWINK PLASTOMETER

P, P'. Plane-parallel plates  
G. Compressing weight  
M. Dial for reading off height of specimen

Sarnow and the ring and ball methods cannot be applied at all, as the resin does not flow under the conditions present in these



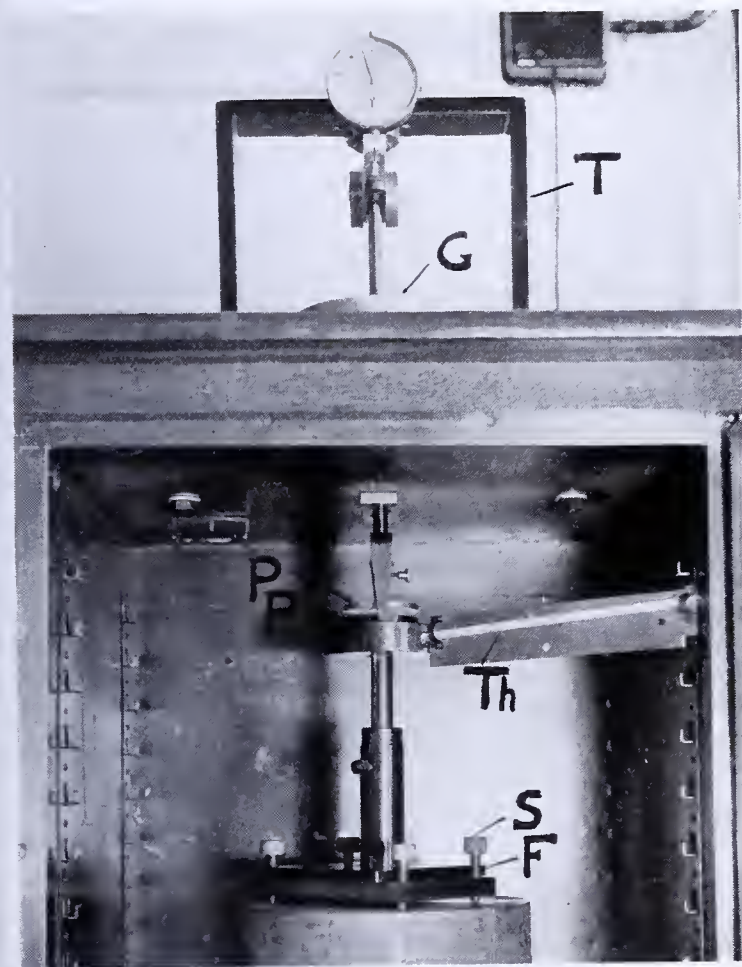


FIGURE 2. PLASTOMETER IN USE

apparatus. Moreover, hardening resins must not be heated close to their melting point, as polymerization will go on. The penetration method leads to erroneous results because of the gas bubbles which cannot be avoided when pouring out hardening resins. With bitumens these bubbles can be driven out by heating for some hours, but this procedure is not permissible with a hardening resin.

Still another reason makes the use of a plastometer extremely attractive. One can preheat the resin specimens at a certain temperature during increasing periods. After each period the hardness can be determined, and the increase of hardness per unit of time is a measure of the hardening velocity of the resin (for the determination of the reaction velocity along more scientific lines, see 3, 4, 8, 9, 13, 15). Working along more scientific lines (see Figure 10) one can calculate the viscosity after each period of preheating and in this way one can obtain a  $\frac{d\eta}{dt}$  curve. As there are reasons for supposing that  $\frac{d\eta}{dt}$  will be some function of the reaction velocity constant  $K$ :

$$\frac{d\eta}{dt} = f(K) \tag{1}$$

this may open in the future a way to determine  $K$ .

**Schopper-Houwink Plastometer**

The plastometer described here is based on the same principles as the well-known Williams plastometer (7, 10, 17) but it has been modified to produce an extremely simple and practical apparatus (available through Louis Schopper, Bayrische Strasse, Leipzig). Its chief characteristics are that those parts which must be handled during operation are outside of the heating oven.

Figure 1 shows the apparatus and Figure 2 gives a picture of the instrument in use, mounted in the oven.

The plastometer is fastened to the oven by means of the metal strip,  $T$ . The lower part of the instrument is conducted through the roof and the footplate,  $F$ , is adjusted on the bottom. Plate  $P^1$  contains a thermometer,  $Th$ , in order to be sure that the compression plates keep the right temperature. Experience has shown that this is essential, for in an air-heated oven there are often small differences in temperature. As the deformation process of a flowing resin is extremely sensitive to temperature (the viscosity coefficient becomes ten times smaller per  $10^\circ\text{C}$ . increase in temperature, 7, p. 135), no reliable results can be obtained if this precaution is neglected.

**ADJUSTING THE APPARATUS.** The weight,  $G$  (5 kg.), is mounted and with the aid of knob  $K$  plates  $P$  and  $P'$  are adjusted plane-parallel to each other. By means of the screws,  $S$ , care is taken that the footplate,  $F$ , "bears" on the bottom of the oven.

**CARRYING OUT A MEASUREMENT.** Two pieces of filter paper are laid between  $P$  and  $P'$  and the dial,  $M$ , is adjusted at zero.  $P$  is levered by means of  $K$  and now the resin cylinder—the height of which has been made exactly 5 mm. on a piece of sandpaper—is put between the filter papers.  $P$  is lowered until the dial indicates 5 mm. Then the time,  $t_0$ , is noted and  $K$  is quickly unscrewed so far that, if necessary,  $P$  and  $P'$  can touch each other. Now one can follow on the dial the change of height of the cylinder per unit of time.

When determining the hardness,  $h_{30}$ , the success of the method depends wholly on the right preparation of the resin cylinder.

For this purpose the specimen,  $H$ , is made as shown in Figure 3. One gram of the pulverized resin is put into  $A$ , after its wall has been covered with a piece of thin parchment paper in order to avoid sticking. The weight,  $B$ , is put on and the whole is heated in an oven at a temperature (sinter temperature, usually between  $60^\circ$  and  $80^\circ\text{C}$ .; it must not be taken too high, as the danger of polymerization will then arise), such that the powder sinters and a homogeneous cylinder is obtained; this can be pushed out of  $A$ .

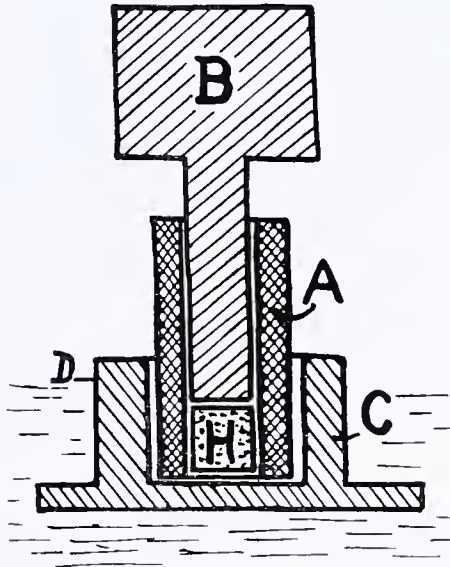


FIGURE 3. APPARATUS FOR MAKING RESIN CYLINDERS AND FOR POLYMERIZING THEM BELOW ABOUT  $80^\circ\text{C}$ .

When only a hardness determination is required, this cylinder can be used for that purpose. If, however, one wishes to determine the hardening velocity of the resin, a polymerization of the resin must be carried through. This can be done in two different ways.

Before pushing the cylinder out of  $A$ , the apparatus of Figure 3 is put in a heated oil bath, the level of which is just below  $D$ . This method can be used only when the reaction temperature is so low that no gas bubbles (foaming) are formed in the resin. When investigating a phenol- or cresol-formaldehyde resin of the resol type at a reaction temperature below about  $80^\circ\text{C}$ ., for example, the conditions for this process are fulfilled.

When reaction temperatures higher than about  $80^\circ\text{C}$ . are to be used—for instance, when investigating a phenol-formaldehyde resin of the novolac type to which hexamethylenetetramine has been added—so much gas will be produced that the resin cylinder



gets spoiled. Then one can let the reaction take place first and afterward make the testing cylinder. For this purpose one gram of the resin is brought into tube *R* and this tube is fastened into holder *H* (Figure 4). A small hole, *L*, remains open, through which the gases to be produced can escape. *H* is then put into a bath (Figure 5) containing a boiling liquid (in the authors' case, butanol, chosen because it is not dangerous or poisonous and does not thicken on prolonged heating. B. p. is  $117.5^{\circ}\text{C.}$ ), so that the polymerization is carried out at a constant temperature. In the thermostat there is room for six holders, *H*. The gas developed makes the resin, which is first melted in the tube, start foaming and spreading all over the surface of the tube, so that an ideal way of heat transfer is guaranteed. This is essential as, because of the short polymerization time (usually between 2 and 10 minutes), the resin can be equally and thoroughly heated only in the form of a thin layer. After polymerization the resin is scratched from tube *R* and the resin test cylinder is made according to the method shown in Figure 3.

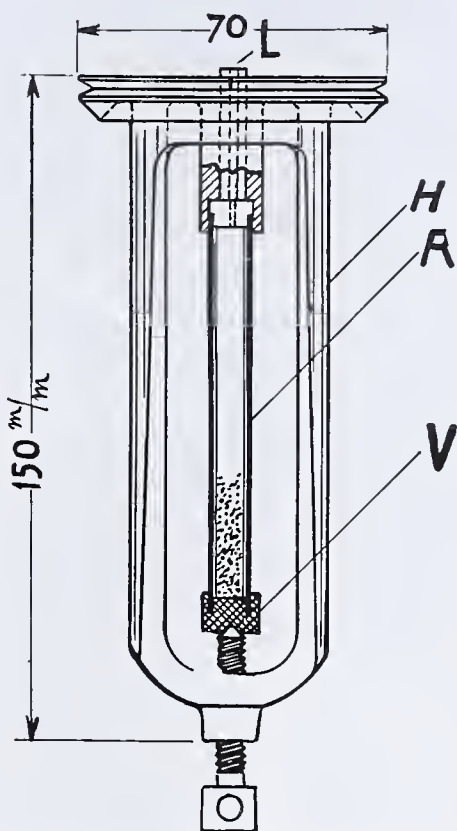


FIGURE 4. APPARATUS FOR POLYMERIZING RESINS AT TEMPERATURES ABOVE ABOUT  $80^{\circ}\text{C.}$

It is possible to vary the reaction temperature at will by taking another boiling liquid in the thermostat. Experiments have shown, however, that the temperature of  $117.5^{\circ}\text{C.}$  is sufficient for a classification of resins with regard to their molding properties. With higher temperatures the reaction time becomes still smaller, leading to relatively greater errors.

### Interpretation of Plastometer Results

There are two ways of interpreting plastometer results.

**PRACTICAL METHOD.** The merely practical method makes use of  $h_{30}$ , the height of the cylinder, measured after 30 minutes' compression, a value which can be taken from Figure 6, being for these two different resins 3.1 and 0.6 mm., respectively. The reaction velocities of two resins can be compared according to this practical method by determining the increase of  $h_{30}$  on heating.

Figure 7 shows the result for two resins, of which I is the softer, being more reactive, however. Some practical applications of this method are given later.

Figure 8 shows the influence of adding various proportions of hexamethylenetetramine, and proves that it is of no use to add more than about 14 per cent in this particular case.

Figure 9 gives a comparison of the reaction velocities of three commercial types of resins, all of the novolac type (16 per cent hexamethylenetetramine added). A special correction has been made here to eliminate the differences in  $h_{30}$  at the beginning. In order to do this the curves have been transported horizontally until they intersect the ordinate at point  $h_{30} = 1.0$  mm. By means of this artifice the resins are brought (at least on paper) into a comparable state of polymerization, characterized by  $h_{30} = 1.0$  mm. Now the slope of the curves measures the velocity by which polymerization proceeds, starting from this fixed state.

**SCIENTIFIC METHOD.** The scientific method makes use of our knowledge (6) that the property which was expressed above by "hardness" is dependent on two physical constants, the viscosity coefficient,  $\eta$ , and the yield value,  $f$ . Of these two constants the yield value, in the case of resins in a state of polymerization as investigated here, is often zero or at least doubtful [6, p. 357 (English ed.), p. 350 (German ed.)]. Under these circumstances it is possible to derive  $\eta$  from the  $\frac{dh}{dt}$  ( $h$  is sample height,  $t$  = time) observations on the plastometer. Scott (14) and Peek (11) have shown that under

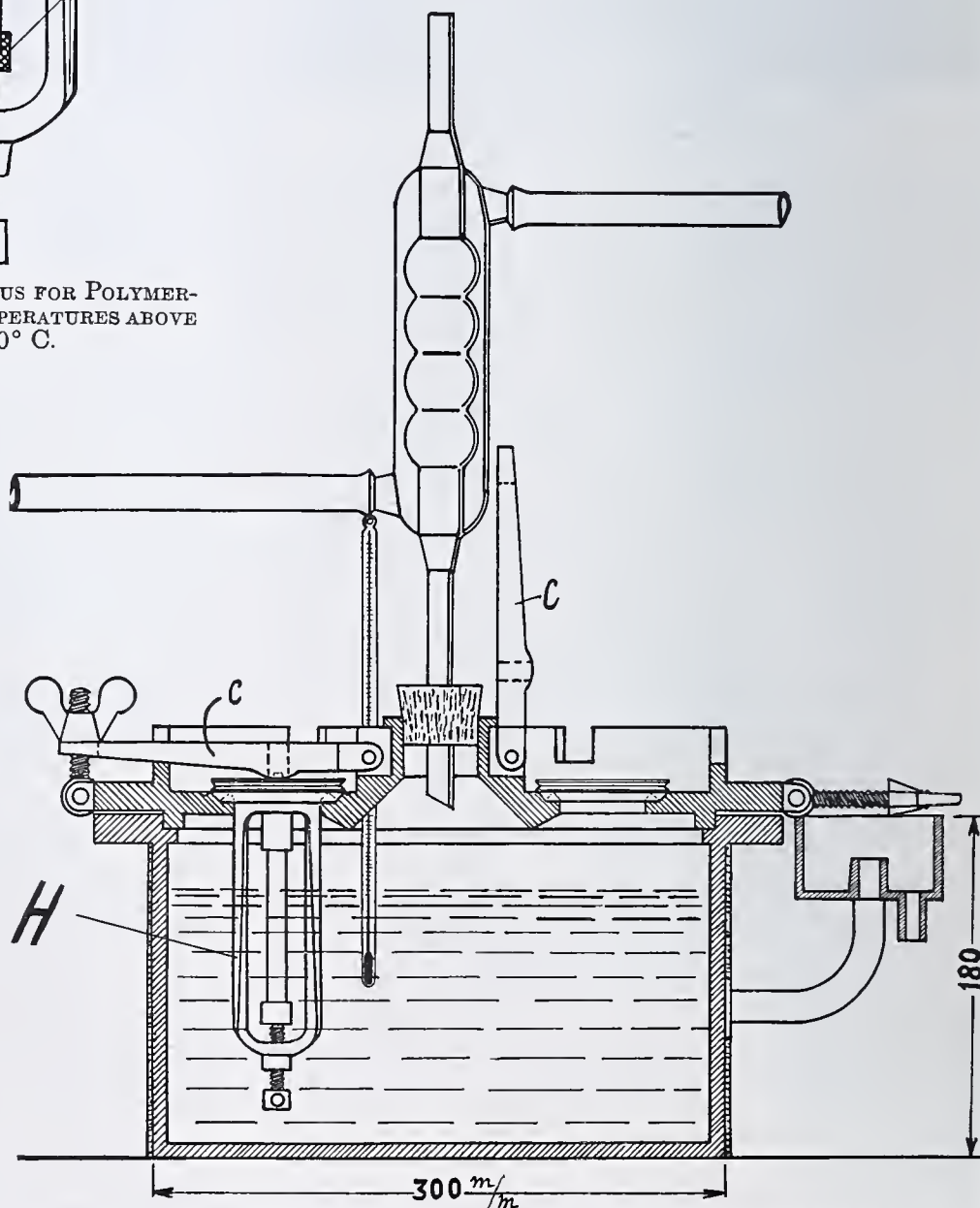


FIGURE 5. THERMOSTAT FOR CARRYING OUT POLYMERIZATION ABOVE  $80^{\circ}\text{C.}$



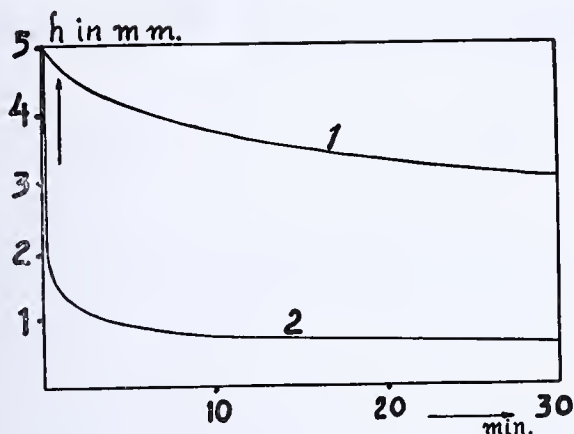


FIGURE 6. RESIN HARDNESS

When height,  $h$ , of specimen is plotted against time of compression, a measure,  $h_{30}$  (height after 30 minutes), can be taken for expressing resin hardness

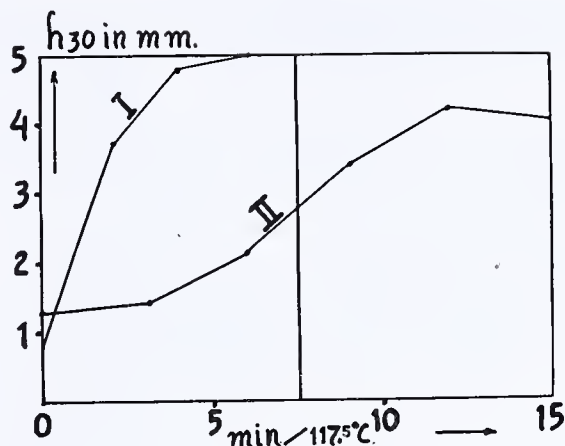


FIGURE 7. RESIN REACTIVITY

A practical way for comparing reactivities of resins I and II is by noting their  $h_{30}$  increase on polymerization. Resin I is more reactive than resin II.

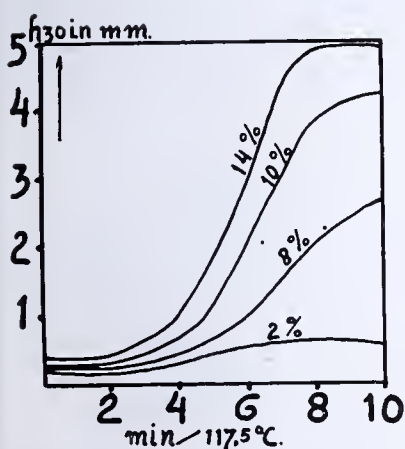


FIGURE 8. INFLUENCE OF HEXAMETHYLENETETRAMINE ON HARDENING VELOCITY OF A PHENOL-FORMALDEHYDE NOVOLAC

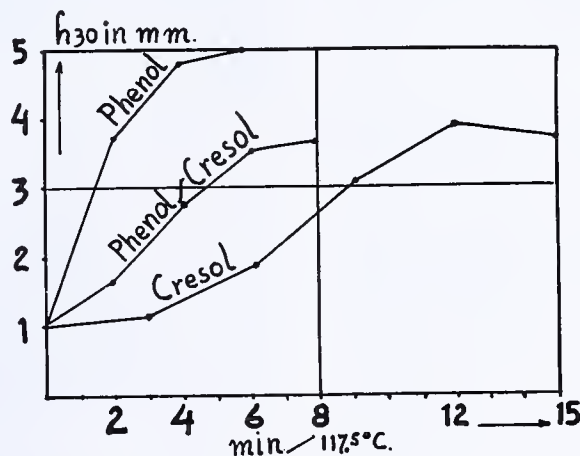


FIGURE 9. COMPARISON OF HARDENING VELOCITIES OF THREE SYNTHETIC RESINS  
Phenol, phenol-cresol, and cresol-formaldehyde resins.  
Curves corrected for constant  $h_{30}$

Plotting, therefore,  $\log \frac{dh}{dt}$  against  $\log h$  one can easily find the value of  $\eta$  in a graphical way. An interpretation of experimental results for more complicated types of flow, such as non-Newtonian flow or when a yield value is present, is given in the literature (7, 11, 14).

In Figure 10 are reproduced some curves showing the increase of  $\eta$  when polymerizing resins of various origins. It appears that metacresol in the present formula (acid condensation with 16 per cent hexamethylenetetramine added afterward) leads to the quickest curing resin. Para-cresol gives a very low quality and phenol is intermediate with regard to its curing properties.

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RECEIVED August 31, 1938.

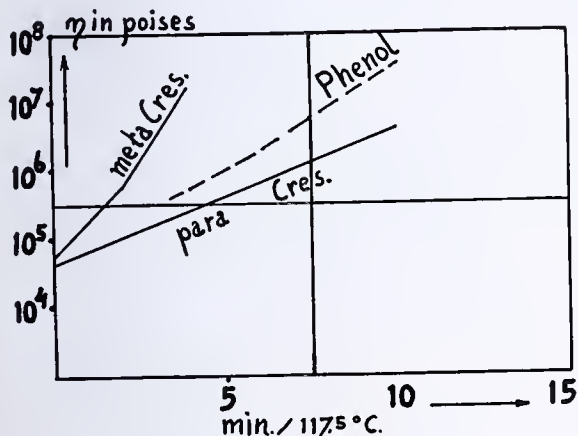


FIGURE 10. COMPARISON OF REACTION VELOCITIES OF THREE SYNTHETIC RESINS

By observing changes in viscosity coefficient on polymerizing

conditions of pure (Newtonian) flow—which often takes place for the resins considered here—the following formula holds:

$$\log \frac{dh}{dt} = \log \frac{2\pi G}{3\eta V^2} + 5 \log h \quad (2)$$

where

$G$  = weight in plastometer  
 $V$  = volume of cylinder of resin



# A Titrimetric Step in Determining Rotenone

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A titrimetric step in the procedure for determining rotenone uses a rotenone-dichloroacetic acid solvate and makes the method a volumetric one. The acid solvate is crystallized quantitatively from solution in the acid by addition of water, separated, and titrated with alkali. As applied to the carbon tetrachloride solvate obtained in the usual crystallization procedure, the method effects a great saving in time, and in accuracy and precision it is equal to the gravimetric method.

THE solvate of rotenone with acetic acid has previously been reported (2). Recently a study was undertaken of the possibility of using an acid solvate such as this as the basis for a method of determination involving titration of the combined acid. Since this particular solvate has a low proportion of acid (2 moles of rotenone to 1 of acetic acid), solvates were sought with other organic acids.

Propionic and alpha-chloropropionic acids were found to combine with rotenone in the same ratio as does acetic acid. Monochloroacetic acid gave a material with a very low percentage of acid of no definite molecular ratio. Trichloroacetic acid may form a solvate containing an equimolecular proportion of rotenone and acid, but in all attempts to prepare it the percentage of acid was slightly higher than this, perhaps owing to tenacious retention of excess acid.

Dichloroacetic acid, however, formed a definite solvate containing 1 mole of rotenone to 1 of acid. It was found possible, by dissolving rotenone in dichloroacetic acid and carefully adding water, to convert the rotenone quantitatively to this acid solvate. On filtering and washing with water, the excess acid was readily removed, and titration of the solvate with standard alkali gave the theoretical percentage of acid for the molecular ratio mentioned. The method has been adapted to determining the purity of the crude carbon tetrachloride solvate obtained in the gravimetric crystallization method (3), and the procedure thus becomes an entirely volumetric one. A saving in time of from 6 hours to 1 day is effected in the determination.

The extraction of the root sample and crystallization from carbon tetrachloride at 0° C. are carried out by the method already published (3). The carbon tetrachloride solvate obtained in this way is filtered and washed by suction as usual. Then, without further drying, it is dissolved in about 25 cc. of acetone in a 250-cc. flask. This is readily accomplished by placing the crucible in a funnel and washing the contents through into the flask with small lots of acetone. The solvent is evaporated completely on the steam bath. The residue is treated with 10 cc. of 80 per cent (by volume) dichloroacetic acid and warmed gently until the residue just dissolves. The solution is then cooled in an ice bath for a few minutes, 10 cc. of cold water are added slowly with swirling, a few seed crystals of rotenone-dichloroacetic acid solvate are added, and the flask is again cooled in the ice bath for 2 or 3 minutes. Separation of a few small needle crystals will usually be noted at this point. If not, water is added a drop or two at a time, with intermittent cooling, until a few crystals are noted.

Water is then added 10 to 15 drops at a time, with about 1 minute's cooling between additions, until 25 cc. have been

added, then 25 cc. more are added dropwise and the solution is again cooled, and finally 50 cc. are added more rapidly and the solution is again cooled. The material is filtered through a Gooch crucible, with filter paper, and washed with about 250 cc. of water in small portions. The outside of the crucible is rinsed with water and the contents are dissolved in 25 cc. of chloroform. This solution may be accomplished by placing the crucible and contents in a beaker, adding the chloroform, and leaving the crucible in the beaker during the titration. To the chloroform solution 50 cc. of freshly boiled water are added, and the mixture is titrated with 0.1 N alkali, with phenolphthalein as indicator. The mixture must be thoroughly agitated, particularly near the end point, to ensure that all the acid is extracted from the chloroform layer.

Each cubic centimeter of 0.1 N alkali is equivalent to 39.4 mg. of rotenone. A blank should be run on the chloroform used. The usual allowances (3) for added rotenone and for solubility in carbon tetrachloride are made—any rotenone added in the original crystallization is subtracted from the result, and 0.07 gram is added to allow for solubility in the 25 cc. of carbon tetrachloride used.

## Discussion of the Method

It was found that, when the carbon tetrachloride solvate was dissolved directly in dichloroacetic acid, the results of the determination were invariably low. When the carbon tetrachloride was removed by evaporation with acetone, correct results were obtained. Consequently, in making determinations on unsolvated rotenone, to which the method is also applicable, the evaporation with acetone is unnecessary.

TABLE I. PURITY OF CARBON TETRACHLORIDE SOLVATES BY ALCOHOL RECOVERY AND BY TITRATION

Sample	Solvate No.	By Alcohol Recovery %	By Titration %
Derris root	1	86.5	88.5, 88, 88, 88, 88
	2	89	90.5, 91, 91
	3	81.5	85, 85
Cube root	4	87.5	90, 91
	5	84.5	86
Pure solvate	6	100	98, 98, 100

Perhaps the most important point in the procedure is that of obtaining actual crystallization of the acid solvate rather than precipitation of an amorphous material. If the latter occurs, excess acid is retained tenaciously. The 10 cc. of water first added are sufficient to make the solution supersaturated in the cold, if the rotenone content is at least 1 gram, as required in the carbon tetrachloride crystallization. After the addition of a seed crystal, sufficient time should be allowed to see that crystals have actually formed. Crystals of the acid solvate for seeding may readily be obtained by dissolving pure rotenone in the 80 per cent acid and slowly adding water. Seeding is not necessary in the determination as slow addition of more water will finally induce the material to crystallize, but it does expedite the procedure. As further water is added slowly, a point is reached, depending on the amount of rotenone present, at which a thick mass of crystalline material separates.

One advantage of the method is that neutral insoluble materials present with the carbon tetrachloride solvate in no way interfere with the determination, as they do in the gravimetric method using the alcohol recovery test. Insecticidal dusts containing sulfur, which is frequently mixed with derris or cube, may be analyzed by this method without interference from the sulfur.



### Results

In tests on specially prepared carbon tetrachloride solvates (Table I), the method gave values for purity about 2 per cent higher than those by the older alcohol recovery test. Since the alcohol recovery test as used in this laboratory is known to give results about 1 per cent lower than the correct value (1), the titration method appears to be at least as accurate.

TABLE II. ROTENONE IN ROOT SAMPLES AS DETERMINED BY THE GRAVIMETRIC AND THE VOLUMETRIC METHODS

Root	Sample No.	Gravimetric Method %	Volumetric Method %
Derris	3002	2.0	2.2, 2.0, 2.0
	3006	3.6	4.0, 3.9, 3.8
	3126	5.8	5.8, 5.7
	3307	7.4	7.2, 7.4
	3307	7.4	7.2, 7.4
Cube	3004	2.9	2.9, 2.9
	3005	5.6	5.6, 5.6
Timbo	3230	3.9	3.8, 3.8

Results of rotenone determinations on samples of powdered root were in good agreement with those by the older gravimetric procedure (Table II). The precision of the method, as judged by the replicate determinations (Tables I and II), appears to be as good as that of the gravimetric procedure.

### Adaptation as a Direct Method

Attempts were made to precipitate the acid solvate from a dichloroacetic acid solution of whole derris and cube extracts. Such a procedure would greatly shorten the determination of rotenone. However, the resinous material formed was difficult to filter and retained excess acid which it was practically impossible to remove entirely. Numerous materials were added to overcome this, but none was satisfactory. Naphthalene was the best of such materials tried, and in one sample gave fair but not consistent results. When samples of higher nonrotenone-resin content were tried, the results were again too high. It is possible that future work will reveal a method for applying this idea directly to whole extracts, but no such procedure can be recommended at present.

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## A Simple Melting Point Outfit

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IN ORGANIC laboratory technique, it is common to take melting points in a beaker while stirring the heated liquid. The outfit herein described is a modification of this well-known procedure.

To make for permanence of setup, greater ease of manipulation, decreased dangers of breakage, and no contamination with rubber, a piece of 4-mm. Pyrex tubing is sealed onto a 400-cc. beaker, as shown in Figure 1. With some care and practice, it is a very simple matter to seal the tube onto the

beaker without blowing. The tube is sealed on at an angle slightly less than 45 degrees to the vertical and is tilted slightly forward, as shown in Figure 2. This slight forward tilt makes certain that the capillaries will be held in place by being gently wedged in between the thermometer bulb, the bottom of the side arm, and the top of the side arm, and does away with using wire springs or constricting the bottom of the side tube. This method

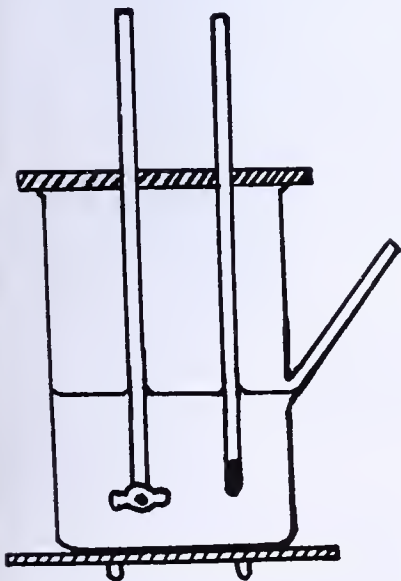


FIGURE 1

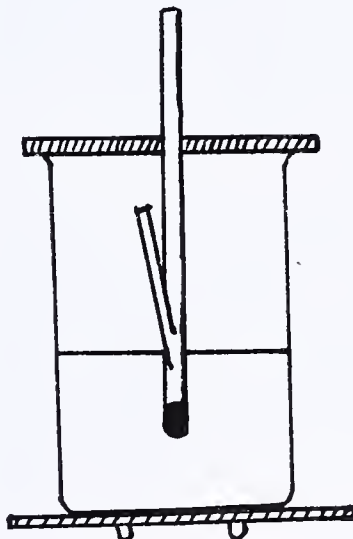


FIGURE 2

also allows several capillaries to be placed one on top of the other, so that several melting points can be taken at one time with only one side tube.

A small electric motor is advantageous, as it gives rapid agitation and is noiseless and inexpensive. Both flywheel and centrifugal stirrers have been used satisfactorily with this type of outfit. For uniform heating, the beaker is supported on a sheet of asbestos.

Cottonseed oil has been found very useful as a liquid for the bath.

It is compounded with 1 per cent of hydroquinone as recommended by Gill and Ebersole (1) and further protected from dirt and rapid decomposition at relatively high temperatures by covering the beaker with a thick sheet of asbestos having two small holes bored for the thermometer and stirrer.

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RECEIVED August 18, 1938.



# Determination of Organic Sulfur

## With Special Reference to Sulfones and Sulfoxides

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AMONG the several available methods for determining organically combined sulfur, insufficient attention has been paid to that originally described by Brunck (1) and applied by him to the analysis of sulfur in coals.

While the usual methods offer no difficulty with many sulfur compounds, compounds containing sulfoxide and sulfone linkages occasionally give inconsistent results. A number of investigators have pointed out the stability of sulfonic acids towards pyrolysis; the Carius method for sulfur has been shown to give uniformly low results on compounds when a sulfonic acid is an intermediate product of decomposition (1, 2, 4). The conventional Parr technique involving combustion in a suitable bomb with sodium peroxide (3) can be made to yield consistent values, but is sensitive to minor variations in manipulation. In addition, the relatively expensive apparatus required is not always available in every laboratory.

In working with a series of substituted sulfonanilides the writer found pronounced difficulty in obtaining satisfactory decomposition. Use of the familiar method of Eschka gave consistently low results, as did attempted fusion with sodium carbonate-potassium nitrate mixtures. Combustion in a Parr bomb gave results which were generally satisfactory but were occasionally quite high.

The method of Brunck, involving a catalytic oxidation of the sulfur-containing compound with a stream of oxygen in the presence of sodium carbonate and cobalt oxide, gave satisfactory values and could be carried out with greater ease than any of the previous methods tried. The sulfur is quantitatively burned to sulfate and may ultimately be determined by precipitation and weighing as barium sulfate. The method possesses the distinct advantage of requiring no apparatus not easily obtained or constructed in the laboratory, and no exacting manipulative technique is involved.

### Apparatus

Details of the relatively simple apparatus required are shown in Figure 1. A 30-cm. (12-inch) length of Pyrex tube, of approximately 2.5-cm. (1-inch) diameter, is fitted with a ground-glass joint at one end; the outlet tube is so arranged as to permit conducting the combustion gases beneath the liquid level in a 600-ml. beaker which contains approximately 300 ml. of 2 per cent sodium carbonate in distilled water. The other end of the combustion tube is connected directly to a suitable mercury valve which acts as a bubble counter; the inlet tube of this valve is connected to the control valve of an oxygen tank. The combustion tube is so arranged that the flame of a Bunsen burner may be played under the far end of the combustion boat, as shown in Figure 1.

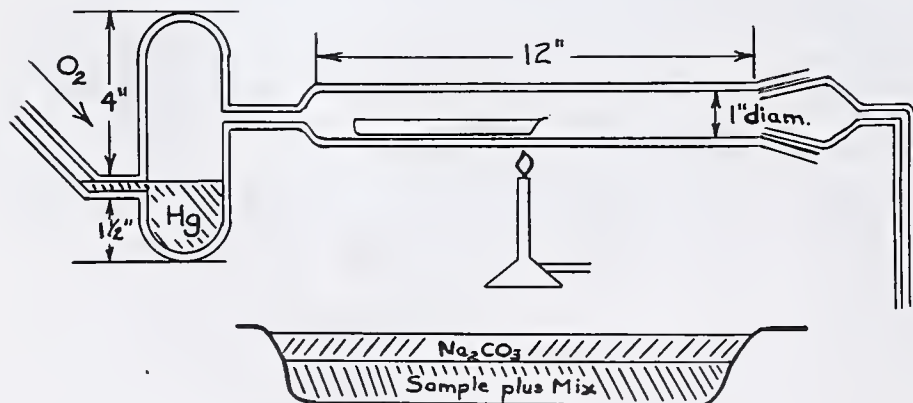


FIGURE 1. DETAILS OF APPARATUS

### Procedure

Approximately 0.5 gram of sample is accurately weighed into a suitable glass mortar; 2 grams of a 1 to 1 mixture of c. p. sodium carbonate and cobalt oxide are added, and the whole is ground together. (The writer has found it advisable to weigh the combustion mixture accurately, as a small correction for possible sulfur in the cobalt oxide may be necessary; this is obtained by running a blank determination, using benzoic acid or other suitable sulfur-free compound as the combustible material.) The sample and combustion mix are transferred to a suitable steel combustion boat by means of a camel's-hair brush, and covered with a layer of anhydrous sodium carbonate (see Figure 1).

Having introduced the charged combustion boat into the tube and assembled the apparatus, a gentle stream of oxygen is turned on, and the medium flame of a Bunsen burner is played beneath the end of the boat away from the oxygen inlet. Within 2 minutes the sample begins to glow; at this point the flame is removed, and the progress of the combustion is regulated by the rate of oxygen flow. After 5 minutes the glow will have traveled the length of the boat and the combustion is complete. Occasionally the charge actually ignites; this does no harm, though considerable carbon may be deposited in the outlet tube.

TABLE I. ANALYSES OF TYPICAL SULFONANILIDES

Compound	Formula	Sulfur	
		Calcd. %	Found %
<i>p</i> -Toluenesulfon- <i>N</i> -anilide			
<i>n</i> -Propyl	C <sub>16</sub> H <sub>19</sub> O <sub>2</sub> NS	11.07	10.98
Isopropyl	C <sub>16</sub> H <sub>19</sub> O <sub>2</sub> NS	11.07	11.09
<i>S</i> -Butyl	C <sub>17</sub> H <sub>21</sub> O <sub>2</sub> NS	10.56	10.44
<i>p</i> -Toluenesulfon- <i>m</i> -toluide			
<i>N</i> -Methyl	C <sub>15</sub> H <sub>17</sub> O <sub>2</sub> NS	11.64	11.61
Ethyl	C <sub>16</sub> H <sub>19</sub> O <sub>2</sub> NS	11.07	11.08
<i>n</i> -Propyl	C <sub>17</sub> H <sub>21</sub> O <sub>2</sub> NS	10.56	10.71
Isoamyl	C <sub>19</sub> H <sub>25</sub> O <sub>2</sub> NS	9.55	9.61
<i>p</i> -Toluenesulfon- <i>p</i> -toluide			
<i>N</i> -Isopropyl	C <sub>17</sub> H <sub>21</sub> O <sub>2</sub> NS	10.56	10.76
Isobutyl	C <sub>18</sub> H <sub>23</sub> O <sub>2</sub> NS	10.09	10.04
<i>n</i> -Amyl	C <sub>19</sub> H <sub>25</sub> O <sub>2</sub> NS	9.55	9.70
Isoamyl	C <sub>19</sub> H <sub>25</sub> O <sub>2</sub> NS	9.55	9.43
<i>p</i> -Toluenesulfon- <i>o</i> -toluide			
<i>N</i> -methyl	C <sub>15</sub> H <sub>17</sub> O <sub>2</sub> NS	11.64	11.31
<i>n</i> -Propyl	C <sub>17</sub> H <sub>21</sub> O <sub>2</sub> NS	10.56	10.69
Isopropyl	C <sub>17</sub> H <sub>21</sub> O <sub>2</sub> NS	10.56	10.61
<i>n</i> -Butyl	C <sub>18</sub> H <sub>23</sub> O <sub>2</sub> NS	10.09	9.82
Isobutyl	C <sub>18</sub> H <sub>23</sub> O <sub>2</sub> NS	10.09	9.95
<i>n</i> -Amyl	C <sub>19</sub> H <sub>25</sub> O <sub>2</sub> NS	9.55	9.49
Isoamyl	C <sub>19</sub> H <sub>25</sub> O <sub>2</sub> NS	9.55	9.70

After cooling, the oxygen stream is turned off, and the combustion boat and contents are introduced direct into the 600-ml. beaker. The charge is dissolved with the aid of a stirring rod and the boat removed after rinsing.

The contents of the beaker are carefully acidified with hydrochloric acid, a few milliliters of bromine water are added, the solution is heated to boiling, the bromine is driven off, and the solution is filtered. The sulfate is precipitated from the hot filtrate with barium chloride in the usual manner.

Data showing the analyses for 18 typical sulfonanilides are summarized in Table I.

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# Standardization of 2,6-Dichlorophenolindophenol with Ferrous Compounds

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IN THE course of investigations it was observed that the presence of ferrous ions in canned fruits and fruit juices interfered with the 2,6-dichlorophenolindophenol titer for ascorbic acid. Tillmans, Hirsch, and Reinshagen (4) used ferrous sulfate in the presence of sodium-oxalate to reduce the indophenol. Although this interference of ferrous ions is known, the recent use of ferrous compounds as basic standards for the indophenol does not appear to be recorded. Tillmans, Hirsch, and Hirsch (3) mention the use of ferrous salts as standards, cautioning that the experiment should be performed in subdued light.

TABLE I. INTERFERENCE OF FERROUS IONS

Acid	Dye Used Ml.	Speed of Reaction
Blank	0.05	Very slow
Citric	0.05	Very slow
Metaphosphoric	2.95	Very rapid
Acetic	0.05	Very slow
Oxalic	2.95	Very rapid
Phosphoric	0.05	Slow
Sulfuric	0.05	Very slow
Hydrochloric	0.05	Very slow
Nitric	0.05	Very slow
Trichloroacetic	0.05	Very slow

The authors feel justified in presenting the present paper, because as late as 1936 (1) the belief was expressed that this interference occurs only in neutral solution. Work in this laboratory indicates that this reaction also occurs in the presence of certain acids. Table I shows the results when 10 ml. of each acid (at concentrations giving a pH of 3.0) and 5 ml. of Mohr's salt solution (1 gram per liter) were titrated with an unknown concentration of 2,6 dye. All solutions show a fading of the pink end point on standing. Only oxalic and metaphosphoric gave a quantitative reaction. The end point in oxalic acid fades rather rapidly. The most accurate end point is regarded as the first pink color which remains for 30 seconds.

TABLE II. STANDARDIZATION OF 2,6 DYE

Standard	Concentration N	Indophenol Ml.	Mg./ml.	Error %
Iodine	0.01057	5.000	0.310	0.00
FeCl <sub>2</sub>	0.00503	5.075	0.316	+1.90
FeSO <sub>4</sub>	0.00359	3.650	0.313	+0.90
Mohr's	0.00255		0.308	-0.64

The use of ferrous ammonium sulfate (Mohr's salt) as a possible convenient basic standard for 2,6-dichlorophenolindophenol has been investigated. The method used is as follows:

Dissolve 1 gram of the ferrous salt in water, add 10 ml. of concentrated sulfuric acid, and make up to 1 liter. To 2 to 5 ml. add 5 to 10 ml. of oxalic acid (saturated, approximately 4 per cent) or metaphosphoric acid (3 per cent). Titrate with the 2,6-dichlorophenolindophenol.

## Results

One mole of the dye (290 grams) is equivalent to two atoms of iron, or the iron equivalent of one mole of the indophenol is 111.68 grams. One mole of the dye oxidizes one mole or 176.064 grams of ascorbic acid. This yields the following equivalents:

- 1 mg. of ascorbic acid  $\approx$  0.000634 gram of Fe<sup>++</sup>
- 1 mg. of ascorbic acid  $\approx$  0.003157 gram of FeSO<sub>4</sub>·7H<sub>2</sub>O
- 1 mg. of ascorbic acid  $\approx$  0.002257 gram of FeCl<sub>2</sub>·4H<sub>2</sub>O
- 1 mg. of ascorbic acid  $\approx$  0.00445 gram of FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O
- 1 mg. of Mohr's salt  $\approx$  0.2247 gram of ascorbic acid

Believing that the titration of ascorbic acid by the indicator and then of ascorbic acid by iodine is the most accurate method of standardization, the authors have used it as giving the correct value of the dye. Table II reports an experiment in which the various ferrous compounds in concentrations of 1 gram per liter have been compared as standards.

TABLE III. COMPARISON OF METHODS

(Iodine-ascorbic acid standard = 0.293 mg. per ml. of vitamin C equivalent of the 2,6 dye)					
Sample	Thio Method Mg./ml.	Error %	Sample	Ferrous Method Mg./ml.	Error %
10 ml. of dye + KI	0.279	-4.4	2 ml. of Mohr's salt solution (1 gram per liter)	0.295	+0.68
	0.279	-4.4		0.299	+2.00
	0.306	+4.4		0.299	+2.00
	0.277	-5.1		0.295	+0.68
	0.284	-3.0		0.290	-1.00

Menaker and Guerrant (2), as well as Buck and Ritchie, have recently presented a method for standardizing the indicator by oxidizing potassium iodide to iodine, which, in turn, is titrated with sodium thiosulfate. Their results show that the thiosulfate method gives values consistently 2 per cent lower than their iodine-ascorbic acid titration. A comparison of the two methods gave the results presented in Table III.

## Summary

The use of ferrous compounds (particularly ferrous ammonium sulfate) in the presence of metaphosphoric acid or oxalic acid is suggested as a basic standard for 2,6-dichlorophenolindophenol.

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# Determination of Sulfur in Surface-Active Agents

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ONE of the best criteria of the quality of any detergent or wetting-out agent of the sulfuric acid ester or sulfonic acid type is the content of organically combined sulfuric anhydride. The methods available for this determination are (a) the Herbig method (6) in which the sample is decomposed with hydrochloric acid and the sulfate is determined in the water layer after extracting the fat with ether; in another sample, the inorganic sulfate is determined by washing the oil layer, dissolved in solvents, with concentrated sodium chloride solution and determining the alkali sulfate in the wash waters. (b) The Herbig method has been mostly superseded by the acid-titration method (4), in which the sample is decomposed with a known quantity of sulfuric acid and the organically combined sulfuric anhydride is calculated from the increase in acidity. (c) The last and most recent method is the ash-gravimetric method (5), which has been adopted as provisional by the American Association of Textile Chemists and Colorists (1), the American Oil Chemists' Society (2), and the American Society for Testing Materials (3). According to this method the pure sulfonated product is first isolated by extracting with solvents over a concentrated solution of salt and then ashed; from the weight of the ash the combined sulfuric anhydride may be calculated.

The first two methods evidently cannot be used in the case of true sulfonates, which are not decomposed by acids under the conditions of the methods. Furthermore, in the case of highly sulfated sulfuric acid esters, these methods are inconvenient, as it takes a long time for complete hydrolysis—sometimes over 10 hours. The ash or third method may be used for sulfonated as well as sulfated products and is satisfactory for the ordinary type of sulfated oils. Unfortunately in the case of highly sulfated oils or the newer sulfonated detergents, such as the sulfated alcohols, sulfonated fatty acid amides, etc. (particularly if it is necessary to use alcohol as one of the solvents in extraction), the extract carries over with it in solution a large amount of salt, which vitiates the results. Every effort to remove the salt from the solvent by filtering, freezing, or dehydrating has been unsuccessful.

The method proposed in this paper is applicable to every type of sulfated or sulfonated organic compound, provided it may be quantitatively extracted with a solvent over concentrated salt solutions. This was true of every such compound investigated that possessed detergency or surface activity. The sodium salt of  $\beta$ -naphthalenesulfonic acid could not be analyzed by this method, since it was soluble in the salt solution and could not be extracted with solvents, but this compound has no value as a detergent and probably very little value, if any, as a wetting-out agent. The new method is convenient and comparatively rapid, and the results are of good precision and accuracy. It is based upon the observation that the sodium or potassium salt of the sulfonated or sulfated product when shaken with a concentrated solution of ammonium chloride or sulfate is quantitatively converted into its ammonium salt and, conversely, the latter is converted into the sodium or potassium salt when shaken with a concentrated solution of the respective chloride or sulfate.

## Procedure

Shake the sample, dissolved in the proper solvent or solvents, repeatedly with a concentrated solution of ammonium chloride until the conversion is complete—about five portions. Wash the solvent layer similarly with a concentrated solution of sodium

sulfate; all the ammonia bound to the organically combined sulfate or sulfonate is quantitatively converted into ammonium sulfate, which passes into the water layer. The latter also contains all the ammonium chloride with which the solvent layer may have been contaminated. The water layer is now analyzed for total ammonia by distillation with excess alkali and for ammonia due to ammonium chloride by analyzing the same solution or an aliquot portion of it for chloride, an analysis which is most conveniently determined volumetrically. The difference represents the ammonia bound by the organic compound; from these data the organically combined sulfuric anhydride may readily be calculated. A duplicate analysis may be made within 3 hours, regardless of the complexity of the sample.

**SALT WASHINGS.** To a mixture of 50 ml. of a concentrated neutral solution of ammonium chloride (about 30 per cent containing some solid salt) and 50 ml. of ether in a 250-ml. separatory funnel, add enough of the sample to yield about 0.5 gram of organically combined sulfur trioxide and shake vigorously until the sample is completely dissolved. If the sample is a solid, it may more conveniently first be dissolved in water, to which the proper amount of ammonium chloride is then added. Add 5 drops of methyl orange indicator and sufficient 0.5 *N* hydrochloric acid until the water layer after settling is faintly pink. Draw off the lower layer and repeat the washing with four 25-ml. portions of the ammonium chloride solution or until conversion into the organic ammonium salt is complete, shaking vigorously each time for about 1 minute. With unknown samples, a duplicate analysis is made and when the ash of the oil layer upon ignition is negligible, complete conversion has taken place. If an emulsion forms during the washings, add 3 ml. of alcohol at a time, mixing gently after each addition, until the emulsion breaks comparatively rapidly and forms two clear, sharp layers. With certain highly sulfonated oils, three layers may form; in that case, either add enough alcohol to cause the middle layer to combine with the ether layer or draw off only the lower water layer. Combine the washes and extract with one or more portions of 25 ml. of ethyl ether (or with equal parts of alcohol and ether where three layers are formed); discard the water layer and wash the solvent layer with two 10-ml. portions of the ammonium chloride solution. Combine the solvent layers and similarly wash with a neutral 25 per cent solution of sodium sulfate (about 35° C.) free from chlorides and containing some solid salt—or until all of the ammonia is transferred to the water layer. (To test for complete conversion at this stage, the wash water is tested for ammonia in the usual way.) Combine the sodium sulfate washes, extract once with 25 ml. of ethyl ether, and wash the latter with two 10-ml. portions of the sulfate solutions which are combined with the other washes. Total ammonia and ammonia as chloride are determined in the combined sodium sulfate washes, as follows:

**TOTAL AMMONIA.** Dilute the sulfate washes exactly to 500 ml. and determine the ammonia by distilling an aliquot portion or 200 ml. in a Kjeldahl flask with about 35 ml. of *N* sodium hydroxide solution, absorbing the liberated ammonia in 25 ml. of *N* sulfuric acid, and determining the loss of acidity of the latter with 0.5 *N* sodium hydroxide solution, using methyl orange as the indicator. To prevent foaming, pumice stone and 20 to 30 ml. of octyl alcohol may be added to the solution before distillation. Total ammonia is given by the following formula, expressed as milligrams of potassium hydroxide:

$$\text{Total ammonia, as mg. of KOH} = \frac{1}{a} (\text{ml. of H}_2\text{SO}_4 \times t_1 - \text{ml. of NaOH} \times t_2)$$

where  $t_1$  and  $t_2$  represent the titers of the acid and alkali, respectively, in milligrams of potassium hydroxide per ml., and  $a$  is the fraction of the solution taken for analysis.

**AMMONIA AS CHLORIDE.** To another 200-ml. portion of the solution, add 0.1 *N* or 0.25 *N* silver nitrate solution, depending upon whether the extract is more or less contaminated with ammonium chloride (if alcohol was used in the extraction, considerable amounts of ammonium chloride will usually be present), until present in some excess (about 5 ml. of 0.1 *N*), stir continually for about 10 minutes or until the precipitate has coagulated well, filter, and wash the filter free from silver nitrate. Add 2 ml. of nitric acid (4 parts of strong nitric acid and 1 part of water, boiled until colorless), 5 ml. of ferric ammonium chloride (saturated solution), and titrate with 0.1 *N* ammonium thiocyanate solution to a definite brown. Standardize the silver nitrate solution against standardized hydrochloric acid, following as



TABLE I. SULFURIC ANHYDRIDE IN SULFATED PRODUCTS

Product	Organically Combined SO <sub>3</sub>					
	Ammonia or New Method			Acid-Volumetric Method		
	I %	II %	Av. %	I %	II %	Av. %
Sulfated oleic acid	3.88	3.85	3.87	3.90	3.98	3.94
Sulfated castor oil	3.92	3.98	3.95	4.26	4.22	4.24
Sulfated tallow	2.53	2.48	2.51	2.54	2.60	2.57
Sulfated blended oil <sup>a</sup>	3.42	3.51	3.47	3.54	3.61	3.58
Highly sulfated castor oil	6.68	6.58	6.63	6.92	7.04	6.98
Sulfated fatty alcohol	6.13	6.24	6.19	6.01	6.16	6.09

<sup>a</sup> Used in spinning rayon.

TABLE II. SULFURIC ANHYDRIDE IN SULFONIC COMPOUNDS

Product	Organically Combined SO <sub>3</sub>					
	Purified Sample		Sample "As Is,"			Av.
	Ammonia or new method, av. %	Ash method, av. %	Ammonia or New Method I %	II %	Av. %	
Fatty acid amide sodium sulfonate	15.9	15.8	4.39	4.38	4.37	
Alkyl naphthalene sodium sulfonate	24.2	24.4	15.9	16.1	16.0	
Alkyl aryl sodium sulfonate	22.6	22.6	7.87	7.80	7.84	
Sulfonated mineral oil	11.7	11.9	11.4	11.9	11.7	

closely as possible the actual test—namely, in the presence of about 200 ml. of a 10 per cent solution of sodium sulfate. The ammonia bound as chloride is calculated as follows:

Ammonia bound as chloride, in mg. of KOH =

$$\frac{1}{a} (\text{ml. of AgNO}_3 - \text{ml. of (NH}_4\text{)SCN} \times E) t_s$$

where  $E$  represents the equivalent of the thiocyanate in terms of the silver nitrate (standardized in a 10 per cent sodium sulfate solution) and  $t_s$  equals the titer of the silver nitrate, expressed in milligrams of potassium hydroxide.

**ORGANICALLY COMBINED SULFURIC ANHYDRIDE.** It is evident, from the formulas for the ammonium salts of sulfuric acid esters and sulfonic acids ( $\text{ROSO}_3\text{NH}_4$  and  $\text{RSO}_3\text{NH}_4$ ), that one mole of ammonia is equivalent to one mole of combined sulfuric anhydride. Hence, the organically combined sulfuric anhydride is readily calculated from the previous data as follows (the ammonia results are given in milligrams of potassium hydroxide):

$$\text{Organically combined SO}_3, \text{ as ester or sulfonic acid, per cent} = \frac{(\text{total ammonia}) - (\text{ammonia as chloride})}{\text{weight of sample}} \times \frac{\text{SO}_3}{10 \text{ KOH}} = 0.1426 \left[ \frac{(\text{total ammonia}) - (\text{ammonia as chloride})}{\text{weight of the sample}} \right]$$

### Experimental

**COMPLETE CONVERSION INTO AMMONIUM ORGANIC SALTS.** To prove that the conversion into the ammonium organic salts was quantitative, sulfated and sulfonated products, including samples of sulfated oleic acid, castor oil, fatty alcohol, sulfonated fatty acid amides, and sulfonated mineral oil, all in the form of their sodium salts, were washed as outlined in the method and a portion of the ether layers was ashed. The ash in each case was negligible.

**COMPLETE CONVERSION INTO SODIUM SALT.** The rest of the ether layers were then washed with sodium sulfate solution and tested for ammonia by distillation with excess alkali. The results were all negative.

**EXTRACTION.** Extraction in each case was quantitative, as shown by the fact that the wash waters after prolonged boiling with strong acid and further treatment with ether gave either negative results or only traces of fatty matter.

**STABILITY OF SULFONATED OIL IN SOLVENT LAYER.** To determine the stability of products of the sulfuric acid ester type (which have a tendency to decompose under neutral or acid conditions) during washing with the salt solutions, samples of a sulfated castor oil, sulfated oleic acid, and a sulfated fatty alcohol were washed as in the procedure and allowed to remain overnight at room temperature. The ether layers upon further washing showed no development of acidity and there was no decrease in the combined sulfuric anhydride.

**DETERMINATION OF AMMONIA AS CHLORIDE.** No difficulty was caused in this determination by the presence of sodium sulfate. The method was tested by neutralizing known amounts of hydrochloric acid in the presence of sodium sulfate and determining the chlorine content.

### Sulfuric Anhydride Content in Sulfuric Acid Esters

The organically combined sulfuric anhydride in commercial samples of sulfuric esters, including a sulfated fatty alcohol, was determined by the new method and compared with the volumetric acid-decomposition method. The results are

given in Table I. There is a satisfactory agreement between the two methods in the case of the sulfated oleic acid and the sulfated alcohol, but with sulfated castor oil and other glycerides the new method yields results that are 0.1 to 0.4 per cent lower. The higher results by the acid-volumetric method were probably due to sulfated glycerol, which apparently is not extracted by the new method. This conclusion was based upon the following experiment: A sample of sulfated castor oil was extracted over a salt solution and the combined sulfuric anhydride determined according to the acid-volumetric method. The result then agreed with that obtained by the ammonia method.

### Sulfuric Anhydride Content of Sulfonic Compounds

In the case of sulfonic compounds, the samples were extracted with ether and alcohol over a concentrated solution of sodium chloride, the solvent was evaporated, and the residue was dried. The residue was then digested in a small quantity of hot alcohol and filtered to free it from salt. The solvent was evaporated and the residue dried to constant weight. The sample of sulfonated mineral oil was analyzed directly, since it was completely soluble in ethyl ether. Part of the purified residue was analyzed for sulfuric anhydride by the new method. Another portion was ashed, treated with 2 ml. of concentrated sulfuric acid, and ignited to constant weight and the sulfate in the residue, determined by precipitation with barium chloride, was compared with that by the ammonia method. The sulfate determined by the ash method represents half of the sulfuric anhydride, in accordance with the following reaction that takes place upon ashing:



Some of the sodium sulfate is reduced to sulfite and sulfide, but these do not interfere with the results, if the ash is finally treated with sulfuric acid. The results obtained with several sulfonic compounds are given in Table II.

### Summary

A new, convenient, and accurate method has been developed for the determination of sulfuric anhydride in sulfuric acid esters and sulfonic compounds. The method is based upon the conversion of the respective compounds into their ammonium salts and determining the ammonia in the latter.

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# Sulfamic Acid as a Standard of Reference in Acidimetry

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Sulfamic acid is a crystalline nonhygroscopic solid, available on the market in any desired quantity at a moderate price. It is a strong acid in aqueous solution and can be titrated with bases, using indicators with transition ranges varying from a pH of 4 to 9. Sulfamic acid is an excellent acidimetric standard of reference and should find widespread use in analytical chemistry. In precision and accuracy it compares well with other acidimetric reference materials. It can be purified and dehydrated easily and thus be obtained in uniform and exact composition.

IN A RECENT publication dealing with sulfamic acid,  $\text{NH}_2\text{SO}_3\text{H}$ , Cupery (2) calls attention to its unusual physical and chemical properties, pointing out that "it is an important addition to the group of commercial acids represented by lactic, acetic, formic, tartaric, oxalic, and similar acids, and should be especially useful for applications in which a highly ionized, nonvolatile acid is desired, or where precipitation of insoluble salts must be avoided." In discussing potential applications of sulfamic acid he states that "it should find extensive use as an analytical reagent" and that "it has previously been recommended as a standard for titrimetric work because it is a nonhygroscopic crystalline acid which gives sharp end points with ordinary titration indicators."

Hoffmann (6) was the first to suggest that sulfamic acid might serve as an acidimetric standard. He found that solutions of sulfamic acid could be titrated with potassium hydroxide and that either phenolphthalein or methyl orange could be employed as indicator. Herboth (5) subsequently recommended sulfamic acid for use in standardizing pharmaceutical solutions, but probably did not have at his disposal pure sulfamic acid. Several obvious misstatements occur in his publication, chief among which is the observation that an insoluble barium salt is precipitated when barium chloride is added to a solution of the acid. This is not in accordance with observations made in this laboratory; moreover, Cupery (2) gives the solubility of barium sulfamate as 34.2 grams per 100 grams of water at 25° C. Since aqueous solutions of sulfamic acid are slowly hydrolyzed in accordance with the equation  $\text{NH}_2\text{SO}_3\text{H} + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4$ , it is highly probable that the precipitate obtained by Herboth was barium sulfate and not barium sulfamate. Herboth also concluded that sulfamic acid as an acidimetric standard is not susceptible to any high degree of precision. In the light of the experimental work reported below, it is again obvious that the discrepancies reported by him are due to the impurity of his materials.

Misuch (7) also investigated sulfamic acid for use as a titrimetric standard. He was able to obtain comparable titers for solutions of sodium hydroxide and sodium carbonate when standardized with hydrochloric and sulfamic acids.

A comprehensive study of the chemistry of sulfamic acid

has been in progress in this laboratory for several years. It was considered advisable to reexamine the usefulness of this acid as a primary standard, especially since it is now available in quantity both in the commercial and c. p. grades (technical grade from the Grasselli Chemicals Department of E. I. du Pont de Nemours & Company). It is the purpose of the present investigation to describe such a study.

## Physical Properties of Sulfamic Acid

Sulfamic acid is a crystalline nonhygroscopic solid melting with decomposition at 205° C. It is highly ionized in aqueous solution, as shown both by conductometric (8) and pH measurements (2). It is indefinitely stable in the solid state at ordinary temperatures, but undergoes slow hydrolysis in solution in accordance with the equation given above. The solubility of the acid in 100 grams of water ranges from 14.68 grams at 0° to 47.08 grams at 80° C. Sulfuric acid greatly decreases its solubility in water, a fact which may be used in its recovery from solution and in its purification (2). The free acid is appreciably soluble in methanol and ethanol, slightly soluble in acetone, and practically insoluble in ether (2). Such nitrogenous solvents as formamide (2) and liquid ammonia (observation in this laboratory) exhibit marked dissolving power for the acid. Many of the inorganic salts of sulfamic acid have been prepared and practically all are soluble in water. Other physical data are presented in detail by Cupery (2).

## Chemical Characteristics of Acidimetric Standards

Sulfamic acid may properly be compared with such existing standards as benzoic and succinic acids, potassium acid phthalate, and potassium biiodate—nonhydrated crystalline compounds which are soluble in water and can be purified by simple recrystallization from water. Only potassium biiodate and sulfamic acid are strongly acidic and capable of use in connection with a group of indicators having transition points over a wide range of pH values. A comparison of the properties of sulfamic acid and potassium biiodate is, therefore, pertinent.

Potassium biiodate has the advantage of a high equivalent weight and, when properly prepared, possesses a definite, known hydrogen-ion content. However, at least three recrystallizations from water are required to attain satisfactory purity. Since it contains a high percentage of iodine, potassium biiodate is not inexpensive. Its solubility in water at ordinary temperatures is low; it is, therefore, difficult to prepare solutions more concentrated than 0.1 molar. Indicators having transition ranges between pH 5 and 9 may be employed. A solution of standard acid can be prepared using potassium biiodate, although this practice is not often followed.

Sulfamic acid has a low equivalent weight (97.17). The properly purified product has a definite known hydrogen-ion content. It is easily purified by a single recrystallization from aqueous solution. The sulfamic acid of commerce is available in any amount at a very modest price. It is readily soluble in water. Indicators with transition ranges between pH 4 and 9 may be employed. Sulfamic acid has thus far not been employed in the preparation of working solutions of known acid strength, although, as indicated by studies now in progress in this laboratory, by suitable procedure the preparation of such solutions might be made practicable.



## Preparation and Purification of Sulfamic Acid

The sulfamic acid used in this investigation was obtained from a number of sources. Commercial samples produced by the sulfolysis of urea were made available through the courtesy of M. E. Cupery of the Experimental Station of E. I. du Pont de Nemours & Company. Samples were prepared in this laboratory for the preliminary work by the sulfolysis of urea (1), and by the action of sulfur dioxide upon hydroxylamine salts (3) and upon acetoxime (9).

Several methods for the purification of the commercial material were tested before a satisfactory and reproducible procedure was evolved. Simple recrystallization from hot water gave products whose hydrogen-ion values were consistently low to the extent of 0.1 to 0.2 per cent. It was apparent that some nonacid impurity was present in very small amounts—water or possibly urea, since the commercial material is made from urea. Recrystallization from a concentrated sulfuric acid solution was next attempted, but in no case was it possible to eliminate all traces of sulfate ion from the product.

If urea or some other basic material were present in the commercial product, it is conceivable that such a compound would be rather firmly fixed by sulfamic acid in the form of a salt and might concentrate in the first crystalline fractions obtained from solution. Working on this theory a 125-gram sample of the crude acid was dissolved in 300 grams of water preheated to 70° C. The solution was filtered three times with consequent lowering in temperature, and each time the material crystallizing from solution (altogether about 25 grams) was discarded. The final filtrate was cooled rapidly to the temperature of an ice-salt mixture and allowed to stand for 20 minutes. The crystals thus formed were removed by suction filtration, and washed with a small quantity of ice water, then twice with cold ethanol, and finally with ether.

The product was air-dried in an open dish for 1 hour, after which it was ground in an agate mortar and stored in a desiccator over Anhydrene. When samples of this material were analyzed, much more accurate results were obtained. This method was therefore adopted for the purification of the four samples used to establish the value of sulfamic acid as an acidimetric standard of reference.

## Standardization of Reference Solution of Barium Hydroxide

A stock solution (18 liters) of barium hydroxide was prepared and standardized using constant-boiling hydrochloric acid prepared according to the method of Foulk and Hollingsworth (4). The barium hydroxide solution was stored in a large delivery bottle and protected from the carbon dioxide of the air by a tube containing Ascarite. Weight burets were used for all titrations and for weighing the hydrochloric acid.

Table I gives the results of this standardization. These show close agreement between individual determinations and the average hydrogen chloride value of the barium hydroxide solution at the beginning and again at the conclusion of this study. Several hundred subsequent titrations of various samples of purified sulfamic acid were carried out, and are reported consecutively with no omissions. Tables II and III were obtained using the same solution of barium hydroxide, which has a sulfamic acid equivalent of 0.010875 gram per gram of barium hydroxide solution required. Vacuum corrections were applied to all weighings of solutions and samples involved in this study.

## Potentiometric Titration of Sulfamic Acid

A series of pH titrations by sodium hydroxide using the glass electrode was carried out in order to demonstrate the strength of sulfamic acid and to determine suitable indicators

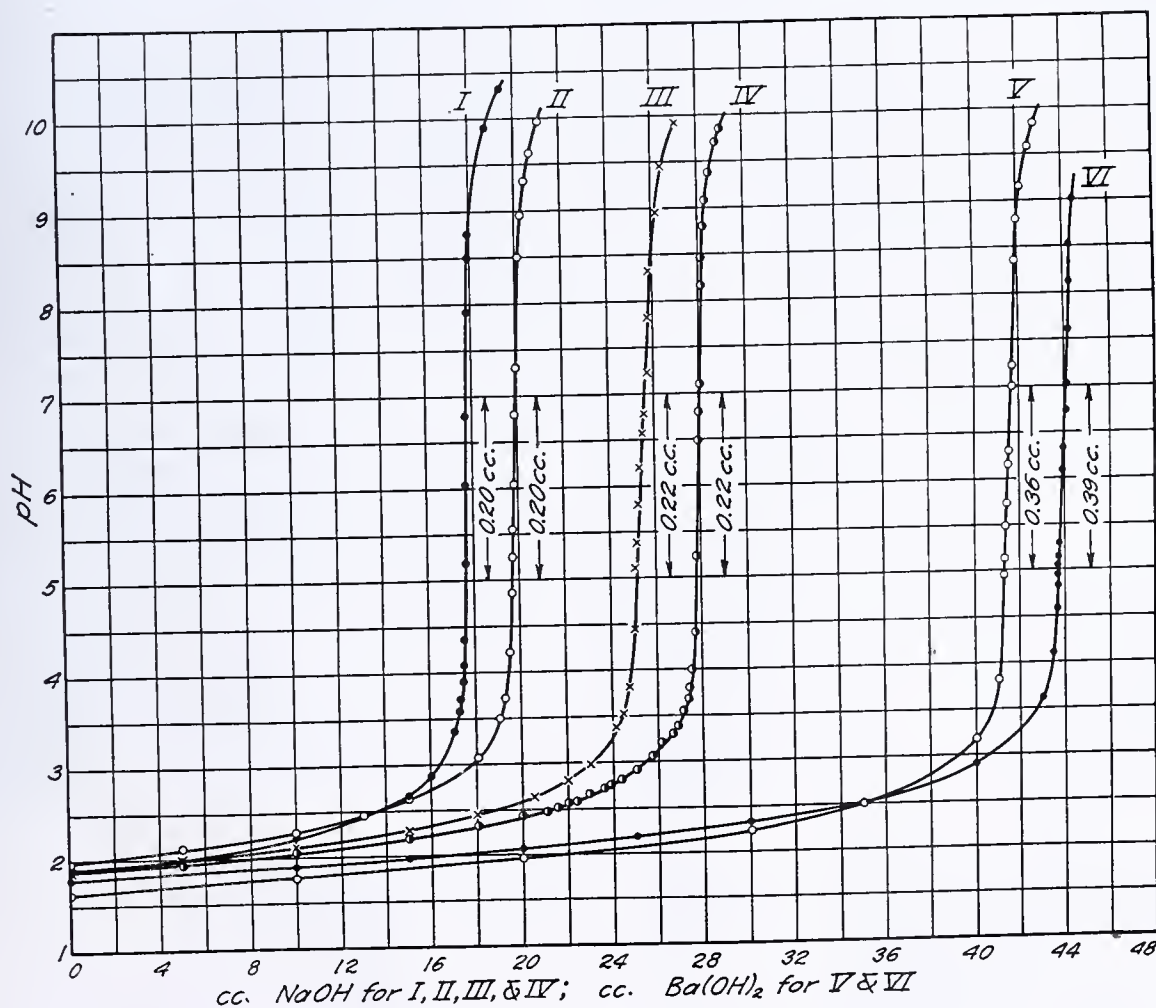


FIGURE 1. TYPICAL TITRATION CURVES

I-IV. Potentiometric titration of sulfamic acid by sodium hydroxide, using glass electrode.  
V, VI. Comparative titrations of hydrochloric acid with barium hydroxide. Sharper breaks continuing over wider pH ranges are obtained with sulfamic acid.



TABLE I. STANDARDIZATION OF APPROXIMATELY 0.1 N BARIUM HYDROXIDE

(Using constant-boiling hydrochloric acid as reference)				
No.	Constant Boiling HCl Gram	Ba(OH) <sub>2</sub> Grams	Gram HCl/Gram Ba(OH) <sub>2</sub>	Deviation from Average %
Standardization at Beginning of Investigation				
1	0.77235	38.284	0.020174	-0.035
2	0.73147	36.206	0.020184	+0.015
3	0.75848	37.552	0.020198	+0.084
4	0.75408	37.363	0.020183	+0.009
5	0.77588	38.494	0.020181	±0.00
6	0.77628	39.498	0.020164	-0.084
7	0.78810	39.039	0.020190	+0.044
8	0.78010	38.666	0.020178	-0.015
Av.	.....	.....	0.020181	0.036
Standardization at Conclusion of Investigation				
1	0.69460	34.409	0.020187	+0.049
2	0.51275	25.362	0.020178	+0.005
3	0.70935	35.187	0.020187	+0.049
4	0.71285	35.346	0.020168	-0.044
5	0.71475	35.443	0.020167	-0.049
Av.	.....	.....	0.020177	0.039

ordinary distilled water was sufficiently low (5.2 to 6) to shift the end point.

Table II gives a typical series of consecutive results. A summary of the average results of four such series is given in Table III. A study of Tables II and III indicates that the average purity of the various preparations is approximately 99.945 per cent. The chief impurity is thought to be water of occlusion. The experimental results show a very satisfactory concordance from a series of individual preparations.

### Discussion

The experimental data demonstrate conclusively that sulfamic acid can serve as an excellent primary standard. The fact that it can be purified merely by recrystallization from water and then need only be dried in air is a strong argument in favor of its use. The slightly low results, as compared with constant-boiling hydrochloric acid, are undoubtedly due to a very small trace of occluded moisture. Drying at 105° C., either at atmospheric pressure or *in vacuo*, did not change the values obtained. Higher temperatures are inadvisable, as samples heated to 135° C. always showed that some of the occluded moisture had been "fixed"—that is, a test for the sulfate ion was always obtained, presumably because of hydrolysis.

Aqueous solutions of sulfamic acid are not stable, as hydrolysis occurs very slowly at room temperatures with formation of ammonium acid sulfate. Since the hydrolytic product contains only one readily releasable proton, it is likely that the titers of such solutions would remain fairly constant. A study of the stability of aqueous solutions of sulfamic acid is in progress.

TABLE II. DETERMINATION OF PURITY OF SULFAMIC ACID

(By titration with standard barium hydroxide using bromothymol blue as indicator. Individual titrational data)

No.	NH <sub>2</sub> SO <sub>3</sub> H		Error		Ba(OH) <sub>2</sub> Gram		Deviation from Average Gram
	Taken Gram	Found Gram	Gram	%	Required Grams	Acid/Gram Base %	
1	0.39340	0.39346	+0.00006	0.02	36.180	0.010873	-0.000005
2	0.39805	0.39783	-0.00022	0.06	36.582	0.010881	+0.000003
3	0.39220	0.39194	-0.00026	0.06	36.040	0.010882	+0.000004
4	0.40245	0.40266	+0.00021	0.05	37.026	0.010869	-0.000009
5	0.39765	0.39737	-0.00028	0.07	36.540	0.010883	+0.000005
6	0.39945	0.39928	-0.00017	0.04	36.715	0.010880	+0.000002
7	0.39065	0.39046	-0.00019	0.04	35.904	0.010884	+0.000006
8	0.39940	0.39944	+0.00004	0.01	36.730	0.010874	-0.000004
Av.	.....	.....	0.00018	0.044	.....	0.010878	0.000005

for its use. A number of typical curves (Figure 1) depict the change in pH on addition of increasing quantities of sodium hydroxide. For purposes of comparison two curves obtained by titrating hydrochloric acid with barium hydroxide are also included. It is readily apparent from the form of these curves that sulfamic acid can properly be classed with the strong acids, and that a whole series of indicators with transition points between pH 4 to 9 can be employed.

Several indicators were used in conjunction with the pH titrations. In the case of bromothymol blue, rosolic acid, phenolphthalein, methyl orange, and methyl red-methylene blue, the characteristic color changes occurred within the indicated pH range.

Bromothymol blue was selected for the subsequent investigation of sulfamic acid because the color change occurs almost exactly at the experimentally determined equivalence point. The color change is also very sharp, yellow at a pH of 6.4 and blue at a pH of 7. This indicator has the disadvantage of giving little warning as the end point is approached. This disadvantage is counterbalanced, however, by the added precision attainable through its use. For rapid but less precise results the mixed methyl red-methylene blue indicator is very useful.

### Standardization of Barium Hydroxide Solution

Approximately 0.4-gram samples of sulfamic acid were weighed in small weighing dishes. Each sample was dissolved in 100 cc. of distilled water contained in a titration flask, and 6 drops of the bromothymol blue indicator were added. Each solution was titrated directly with barium hydroxide from a weight buret. Carbon dioxide-free air was bubbled through the solution during the titration. It was found necessary to use boiled distilled water for washing down the sides of the flask, as the pH of the

TABLE III. DETERMINATION OF PURITY OF SULFAMIC ACID

(By titration with barium hydroxide, using bromothymol blue as indicator. Composite titrational data)

Sample	No. of Dets.	Average NH <sub>2</sub> SO <sub>3</sub> H		Average Error		Average Ba(OH) <sub>2</sub> Required Grams	Average Gram Acid/Gram Base	Average Deviation from Average Gram
		Taken Gram	Found Gram	Gram	%			
A	5	0.40358	0.40326	-0.00032	0.08	37.101	0.010878	-0.000001
B	9	0.40053	0.40037	-0.00016	0.04	36.815	0.010880	+0.000002
C	8	0.40110	0.40099	-0.00011	0.03	36.123	0.010878	-0.000001
D	8	0.39665	0.39655	-0.00010	0.04	36.465	0.010878	-0.000001
Av.	.....	.....	.....	0.00018	0.047	.....	0.010879	.....

### Acknowledgment

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# Precipitation of Nickel and Cobalt Sulfides in a Crystalline State

By Hydrogen Sulfide in the Presence of Pyridine<sup>1</sup>

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IN THE separation of nickel and cobalt from calcium, magnesium, and alkalies, nickel is generally precipitated by ammonium sulfide (3). This method, however, has a number of drawbacks, which are the source of errors and make slower the course of the analysis: (1) Nickel and cobalt sulfides are precipitated in an amorphous state, and because of a strongly developed surface have a great adsorbing capacity; (2) the filtration proceeds slowly; (3) nickel and cobalt sulfides (particularly the former) easily form colloidal solutions, which pass through the filter; and (4) when carbonate is contained in ammonium sulfide, alkaline earth metals may precipitate with the sulfides.

One of the most convenient methods is electrolysis with a mercury cathode. But in the case of the salts, when the amount of nickel and cobalt is large, the deposition of the metal continues for rather a long time, sometimes is not complete, and, in addition, it is necessary to purify large amounts of mercury.

The most desirable method was to precipitate nickel and cobalt in a crystalline form in order to minimize adsorption, to obtain the separation in one precipitation without resort to reprecipitation; and to accelerate the process of filtration.

Haring and Leatherman and Haring and Westfall (1, 2) give directions concerning the precipitation of nickel and cobalt sulfides in the dense modification in a solution of definite pH, ammonium acetate being used as a buffer. However, these authors note that the sulfide precipitates obtained were readily oxidized when exposed to air, while they found it impossible to wash the cobalt sulfide precipitate, because of rapid oxidation.

The present author proposes a new method of precipitating nickel and cobalt sulfides, based on the fact that from the pyridine-containing solution hydrogen sulfide precipitates nickel and cobalt sulfides as a lustrous crystalline precipitate, which settles quickly, and filters very easily. Owing to its crystalline structure the precipitate has a minimum adsorption capacity and is practically not oxidized at all during filtration. Moreover, pyridine does not form any carbonates, and the possibility of the alkaline earth being coprecipitated as carbonates with the sulfides is eliminated.

The process of sulfide precipitation in the crystalline form is unquestionably influenced by the pH of the solution, established by the addition of definite amounts of pyridine, but the pyridine itself also exercises a certain specific influence, resulting in the formation of coarsely crystalline precipitates, very slowly oxidizable during filtering.

## Experimental

For his experiments the author used solutions of nickel and cobalt chlorides, the titer of which had been previously established gravimetrically.

If to a neutral solution of a nickel or cobalt salt, heated to boiling, a pyridine solution is added, and hydrogen sulfide is then passed in, nickel and cobalt are quantitatively precipitated as sulfides in a crystalline state. Nickel sulfide is obtained in larger crystals than cobalt sulfide. Tests carried

out in the presence of ammonium salts have shown that the latter exercise no influence upon the precipitation of the sulfides.

If feebly acid solutions of nickel and cobalt are neutralized by a 20 per cent pyridine solution against methyl red as an indicator and then heated to boiling, an excess of pyridine is added, and hydrogen sulfide is passed in, the sulfides are precipitated in larger crystals than when a neutral solution is used. A study of this phenomenon has shown that the presence in the solution of a pyridine salt favors the formation of larger crystals of sulfides, especially in the case of cobalt sulfide.

A lowering of the pH of the solution in which the precipitation of sulfides is carried on seems to favor the formation of crystals. The influence of the pyridine salt may be accounted for by its buffer action in lowering the pH of the solution, to which free pyridine is added. However, the neutralization of the acid solution by pyridine is difficult, owing to the coloration of the cobalt and nickel solutions. Therefore the author added to the neutral or very feebly acid solution analyzed a solution of pyridine salt obtained by neutralizing a definite amount of acid by pure pyridine to an orange color against methyl red.

After having established the completeness of the precipitation of nickel and cobalt under various conditions of temperature and amount of reagents added, and having obtained good results, the author began experiments on the separation of nickel and cobalt from calcium, magnesium, and alkalies. For these experiments, definite volumes of metal salt solutions were used, the titers of which had been previously determined gravimetrically.

To the neutral or feebly acid solution in an Erlenmeyer flask a solution of the pyridine salt of hydrochloric acid was added (obtained separately by neutralizing 0.5 ml. of hydrochloric acid sp. gr. 1.12, diluted with 25 ml. of water, with pure pyridine, using methyl red as an indicator). After this, the solution was diluted with water to about 150 ml. and heated to boiling. Then about 5 ml. of a 20 per cent pyridine solution were added, and hydrogen sulfide was passed in for about 15 minutes with frequent shaking.

The nickel and cobalt were quantitatively precipitated as crystalline sulfides. The precipitate sometimes adheres to the walls of the flask, and after standing exposed to air it is rather difficult to remove this film from the wall of the vessel. Therefore before starting the filtration, a piece of ash-free filter paper was placed in the flask and was used to remove the sulfide precipitate adhering to the walls, with the aid of a glass rod. The precipitate was then filtered off and washed with hydrogen sulfide water. Nickel sulfide was placed, together with the filter paper, in a flask and dissolved while being heated in nitric acid, the solution was diluted with water and filtered off, and the nickel was then precipitated by dimethylglyoxime as usual. The cobalt sulfide precipitate, together with the filter paper, was carefully ashed in a weighed porcelain crucible, gently heated, and converted to sulfate by evaporating with sulfuric acid. The sulfate was first heated on an electric plate; then the crucible with the cobalt sulfate was placed in another larger porcelain crucible on an asbestos ring, carefully ignited for about 40 minutes with a dull red heating of the bottom of the external crucible, and finally weighed as cobalt sulfate.

In the filtrates from sulfides, after acidulating them with hydrochloric acid and boiling to remove the hydrogen sulfide, calcium, magnesium, and alkalies were determined. Calcium and magnesium were determined in the usual way: calcium, by pre-

<sup>1</sup> Translated into English by A. S. Brashnina.



TABLE I. SEPARATION OF NICKEL AND COBALT

Experiments	Taken				Found				Error			
	NiO Gram	CoO Gram	CaO Gram	MgO Gram	NiO Gram	CoO Gram	CaO Gram	MgO Gram	NiO Gram	CoO Gram	CaO Gram	MgO Gram
1	0.0537	....	0.0531	....	0.0536	....	0.0532	....	-0.0001	....	+0.0001	....
2	0.0537	....	0.0531	....	0.0537	....	0.0533	....	0.0000	....	+0.0002	....
3	0.0537	....	0.0531	....	0.0536	....	0.0530	....	-0.0001	....	-0.0001	....
4	0.0537	....	....	0.0508	0.0537	....	....	0.0508	0.0000	....	....	0.0000
5	0.0537	....	....	0.0508	0.0536	....	....	0.0508	-0.0001	....	....	0.0000
6	0.0537	....	....	0.0508	0.0536	....	....	0.0508	-0.0001	....	....	0.0000
7	....	0.0504	0.0531	....	....	0.0505	0.0533	....	....	+0.0001	+0.0002	....
8	....	0.0504	0.0531	....	....	0.0503	0.0530	....	....	-0.0001	-0.0001	....
9	....	0.0504	0.0531	....	....	0.0506	0.0529	....	....	+0.0002	-0.0002	....
10	....	0.0504	....	0.0508	....	0.0504	....	0.0507	....	0.0000	....	-0.0001
11	....	0.0504	....	0.0508	....	0.0503	....	0.0508	....	-0.0001	....	0.0000
12	....	0.0504	....	0.0508	....	0.0505	....	0.0509	....	+0.0001	....	+0.0001

TABLE II. SEPARATION OF POTASSIUM AND SODIUM

Experiments	Taken				Found				Error			
	NiO Gram	CoO Gram	Na <sub>2</sub> O Gram	K <sub>2</sub> O Gram	NiO Gram	CoO Gram	Na <sub>2</sub> O Gram	K <sub>2</sub> O Gram	NiO Gram	CoO Gram	Na <sub>2</sub> O Gram	K <sub>2</sub> O Gram
1	0.0537	....	0.0527	....	0.0537	....	0.0526	....	0.0000	....	-0.0001	....
2	0.0537	....	0.0527	....	0.0538	....	0.0529	....	+0.0001	....	+0.0002	....
3	0.0537	....	0.0527	....	0.0536	....	0.0528	....	-0.0001	....	+0.0001	....
4	0.0537	....	....	0.0512	0.0536	....	....	0.0513	-0.0001	....	....	+0.0001
5	0.0537	....	....	0.0512	0.0538	....	....	0.0514	+0.0001	....	....	+0.0002
6	0.0537	....	....	0.0512	0.0537	....	....	0.0513	0.0000	....	....	+0.0001
7	....	0.0504	0.0527	....	....	0.0506	0.0529	....	....	+0.0002	+0.0002	....
8	....	0.0504	0.0527	....	....	0.0503	0.0528	....	....	-0.0001	+0.0001	....
9	....	0.0504	0.0527	....	....	0.0504	0.0529	....	....	0.0000	+0.0002	....
10	....	0.0504	....	0.0512	....	0.0503	....	0.0514	....	-0.0001	....	+0.0002
11	....	0.0504	....	0.0512	....	0.0504	....	0.0511	....	0.0000	....	-0.0001
12	....	0.0504	....	0.0512	....	0.0504	....	0.0514	....	0.0000	....	+0.0002

precipitating with ammonium oxalate; magnesium, by the phosphate method after adding ammonium chloride. Pyridine which is in solution not only does not interfere with the precipitation but seems even to favor the formation of more coarsely crystalline precipitates both of calcium oxalate and of magnesium ammonium phosphate.

To determine the alkalis, the filtrates from sulfides were evaporated in Pyrex beakers to remove hydrogen sulfide and then on a water bath in platinum dishes, until a constant volume had been reached. After careful evaporation to dryness on an electric plate the residues were gently ignited but not to red heat. The residues were leached with hot water, and the solutions were filtered off from the carbon into a weighed platinum dish, evaporated on a water bath with 2 to 3 drops of sulfuric acid, and then gently ignited until the excess of sulfuric acid was expelled.

The results of the experiments on the separation of nickel and cobalt from calcium and magnesium are given in Table I, and on the separation of potassium and sodium, in Table II. As shown by the experiments cited in the tables, the results obtained are satisfactory.

The flasks in which the precipitation of sulfides is carried on should be well washed with a chromic-sulfuric acid mixture immediately before the precipitation. This considerably decreases the adhesion of sulfides to the walls of the vessel.

### Practical Directions

This method may be very conveniently applied to filtrates obtained in the separation, with the aid of pyridine, of the subgroup of iron from bivalent metals of the third analytical group, and alkaline earths, magnesium, and alkalis (4, 5, 6).

To precipitate cobalt and nickel, the filtrate is heated, a solution of pyridine salts is added, and the filtrate is treated with hydrogen sulfide.

If the solution is acid, and no determination of alkalis is required, it is neutralized with a solution of sodium carbonate until a turbidity is developed which is cleared by a few drops of dilute hydrochloric acid, and a pyridine salt solution is added (see above). The solution is now heated to boiling and 5 to 10 ml. of a 20 per cent aqueous pyridine solution are added according to the approximate proportion of 5 to 6 ml. to 0.1 gram of nickel or cobalt (a moderate excess of pyridine is not objectionable) and, with a volume of about 150 to 200 ml., hydrogen sulfide is passed in to precipitate the nickel or cobalt.

If alkalis should be determined in the filtrate, the excess of acid is removed by evaporating on a water bath. If the concentration of cobalt or nickel salts is low, the solution may be neutralized with ammonium in the presence of a methyl red indicator until

a yellow coloration develops, and then acidulated with dilute hydrochloric acid until a pink coloration of the indicator appears.

The separation proceeds very smoothly and rapidly, and the precipitate is readily filtered and washed. If in the solution other metals are present, such as zinc, iron, lead, copper, bismuth, and cadmium, they are also precipitated as sulfides.

### Conclusions

The new method worked out by the author for the separation of nickel and cobalt from calcium, magnesium, and alkalis is based on the precipitation of nickel and cobalt sulfides in a crystalline state from solutions containing pyridine. The ammonium salts do not exercise any influence. The presence in the solution of pyridine salt favors the formation of larger crystals. The separation is very clean since the sulfides in the crystalline form possess a minimum adsorption capacity, and the precipitate settles well and is very rapidly filtered. The crystalline sulfides are oxidized only very slowly and do not produce colloidal solutions; therefore the precipitate does not pass through the filter. The method may be used in the analysis of various materials; in particular, the author has used it for the determination of alkalis in nickel and cobalt salts. The use of the method simplifies and accelerates the analysis, without creating any difficulties and without requiring any special apparatus.

### Acknowledgment

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# Separation of Cobalt and Nickel from Manganese

## By Hydrogen Sulfide in a Solution Containing Pyridine and the Pyridine Salt of Hydrochloric Acid<sup>1</sup>

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THE separation of cobalt and nickel from manganese often involves considerable difficulties. The workers of this laboratory had occasion to face this when analyzing asbolane, a mineral containing about 15 per cent of cobalt, 10 per cent of nickel, and 45 per cent of manganese. The usual method of precipitating sulfides of cobalt and nickel in an acetic acid medium (1) does not secure a good separation. Using the method of Hampe the authors failed to secure a complete separation of manganese from nickel and cobalt because of the strongly pronounced adsorptive capacity of hydrated manganese dioxide. Neither did the use of electrolysis give positive results, owing to the formation of very large amounts of hydrated manganese dioxide.

The impossibility of securing a complete separation of cobalt and nickel from manganese by the above methods induced the authors to search for a new method.

In another (3) a new method has been proposed for the precipitation of cobalt and nickel in the form of sulfides by hydrogen sulfide from a solution containing pyridine. Cobalt and nickel separate as a crystalline precipitate, easily filtered and washed. It would be very desirable to find conditions for the precipitation of these metals under which the manganese would quantitatively remain in the solution. From a heated solution containing manganese, hydrogen sulfide in the presence of pyridine causes the formation of a compact gray-green precipitate of manganese sulfide; however, the precipitation does not take place quantitatively. As a result of numerous experiments the authors have been convinced that neither pyridine nor ammonium chloride in any amount holds manganese completely in solution.

A different result is obtained when a pyridine salt of hydrochloric acid is added to the solution analyzed. In this case when the solution is treated with hydrogen sulfide, manganese is not precipitated at all. The action of the pyridine salt of hydrochloric acid may be accounted for in the following manner: (1) The pyridine salts, being added to the solution containing pyridine, lower the pH value of the solution due to its buffer action, thus creating a medium with a too high acidity for manganese sulfide to precipitate. (2) The existence of complex compounds of pyridine with manganese salts is very probable. It is likely that complex compounds of manganese with pyridine (or the pyridine salt of hydrochloric acid) are formed, which, however, are not very stable and the existence of which is limited by a definite pH value of the solution.

### Experimental

For their experiments the authors have used solutions of metal salts, the titer of which was established by the gravimetric method. In the following experiments on the separation of cobalt and nickel from manganese approximately equal amounts of the metals were taken.

To the neutral or weakly acid solution to be analyzed, with a volume of about 200 ml., a solution of the pyridine salt of hydro-

chloric acid was added (5 ml. of hydrochloric acid, specific gravity 1.19, were diluted with 20 to 25 ml. of water and neutralized with pure pyridine, using methyl red as an indicator). Then the solution was heated to boiling, 5 to 10 ml. of a 20 per cent pyridine solution were added, and hydrogen sulfide was passed, with shaking, into the hot solution during 10 to 15 minutes. The cobalt or nickel sulfide precipitated in crystalline form was filtered off and washed with hydrogen sulfide water containing a few drops of pyridine. The nickel sulfide was dissolved in nitric acid, and the nickel was determined by means of dimethylglyoxime. Cobalt sulfide was gently heated to the oxide which was dissolved in sulfuric acid; the excess of acid was removed on an electric plate, and cobalt sulfate was carefully ignited in a double crucible, and weighed. In the filtrates from cobalt and nickel sulfides, manganese was precipitated as ammonium manganese phosphate and determined as pyrophosphate.

The presence of pyridine in the solution favors the formation of a crystalline precipitate. The results are given in Table I.

TABLE I. SEPARATION OF COBALT AND NICKEL

Taken			Found			Error		
CoO	NiO	MnO	CoO	NiO	MnO	CoO	NiO	MnO
Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram
0.0508	....	0.0660	0.0506	....	0.0658	-0.0002	....	-0.0002
0.0508	....	0.0660	0.0510	....	0.0660	+0.0002	....	0.0000
....	0.0529	0.0655	....	0.0527	0.0654	....	-0.0002	-0.0001
....	0.0529	0.0655	....	0.0526	0.0652	....	-0.0003	-0.0003

Table I indicates that the results obtained are satisfactory. Then the authors determined the amount of manganese adsorbed by cobalt and nickel sulfides with varying amounts of cobalt, nickel, and manganese. The volumes of the solutions were about 200 to 300 ml. The procedure remained unchanged; the cobalt and nickel sulfides were gently ignited in a porcelain dish, the oxides produced were fused with potassium hyposulfate, and the amounts of manganese adsorbed by the residue of sulfides were determined colorimetrically with ammonium persulfate and silver nitrate. The results are given in Table II.

TABLE II. MANGANESE ADSORBED

CoO	Taken NiO	MnO	MnO Adsorbed
Gram	Gram	Gram	Gram
0.0005	0.0005	0.1000	0.00003
0.0005	0.0005	0.1000	0.00005
0.0005	0.0005	0.1000	0.00005
0.0050	0.0050	0.0500	0.00004
0.0050	0.0050	0.0500	0.00003
0.0050	0.0050	0.0500	0.00003
0.0500	0.0500	0.0500	0.00003
0.0500	0.0500	0.0500	0.00004
0.0500	0.0500	0.0500	0.00005
0.1000	0.1000	0.0050	0.00004
0.1000	0.1000	0.0050	0.00003
0.1000	0.1000	0.0050	0.00003
0.1000	0.1000	0.0005	0.00000
0.1000	0.1000	0.0005	0.00000
0.1000	0.1000	0.0005	0.00000
0.1000	0.1000	0.0005	0.00000
0.1000	0.1000	0.1000	0.00003
0.1000	0.1000	0.1000	0.00003
0.1000	0.1000	0.1000	0.00004

<sup>1</sup> Translated into English by A. S. Brashnina.



The method developed by the authors secures a complete separation of cobalt and nickel from manganese with widely varying proportions of the metals. The adsorption of manganese is so insignificant that a complete separation is achieved by one precipitation.

### Notes

Cobalt and nickel sulfides sometimes adhere to the wall of the flask, forming a lustrous film; to avoid this, the flask or beakers in which the precipitation of sulfides is carried out should be well washed immediately before this operation. In this way the adhesion of sulfides to the walls of the flask is considerably diminished.

If acid solutions are to be dealt with, they are neutralized with a sodium carbonate solution until the appearance of turbidity, which is subsequently eliminated with the aid of a few drops of dilute hydrochloric acid.

It is convenient to use the filtrates obtained after the separation of the iron, aluminum, and chromium from manganese, cobalt, nickel, etc. by pyridine (2, 4, 5). If the volume is not large, the separation may be carried out after the addition of the pyridine salt and heating.

The method has been verified in the analysis of samples I and II of asbolane. The results of duplicate tests are given:

	I	II
CoO, %	14.45, 14.38	0.17, 0.18
NiO, %	11.34, 11.30	6.19, 6.18
MnO, %	34.22, 34.30	48.51, 48.60

The method may be applied to various products, such as metals, ores, different catalysts used in organic chemical industry, etc.

### Summary

The authors have developed a new method for the separation of cobalt and nickel from manganese, based on the fact that from a hot solution containing a pyridine salt of hydrochloric acid and free pyridine, hydrogen sulfide quantitatively precipitates sulfides of cobalt and nickel in a crystalline state, while all the manganese remains in the filtrate. The sorption of manganese by sulfides of cobalt and nickel is so insignificant that with the most variable proportions of the above metals a complete separation may be secured as a result of a single precipitation.

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## A New Catalyst for the Determination of Nitrogen by the Kjeldahl Method

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THE use of catalysts as digestion accelerators in the Kjeldahl method for total nitrogen has long been known. Numerous investigators have suggested the use of mercuric oxide (4), selenium (1), copper selenite (3), mercuric oxide and selenium (2), and various others, alone and in combination.

The catalyst herein described consists of equal parts of ferrous sulfate and selenium. A search of the literature failed to show that this combination had ever been used. Its practical value has been demonstrated by a large number of determinations, and its effectiveness is of the order of copper sulfate and selenium.

TABLE I. ANALYSIS OF PURE COMPOUNDS

	Theoretical Nitrogen %	Nitrogen Found %	Difference %	Digestion Time	
				CuSO <sub>4</sub> + Se Min.	FeSO <sub>4</sub> + Se Min.
Acetanilide	10.37	10.33	-0.04	26	20
m-Nitrodiphenylamine	16.75	16.71	-0.04	35	30
p-Chloroacetanilide	8.26	8.23	-0.03	37	30
Dinitrobenzene	16.67	16.62	-0.05	28	23

The possibility of the presence of nitro nitrogen in the samples made it necessary to use sulfuric-salicylic acid as a digestion medium. The following procedure was used:

The sample was digested in the cold for 15 minutes with 35 cc. of sulfuric acid containing 1 gram of salicylic acid, 5 grams of

anhydrous sodium thiosulfate were added, and the mixture was heated gently for 5 minutes. The flame was withdrawn and the flask allowed to cool somewhat before adding 10 grams of potassium sulfate and 0.5 gram of catalyst (equal parts of ferrous sulfate and selenium). Heating was then continued until the mixture cleared. The contents of the flask were given an hour afterboil. A blank determination was made on the materials used, and the necessary correction applied to the calculations. Distillation was carried out in the usual manner.

To ascertain whether any nitrogen was lost during digestion, several pure compounds were analyzed using ferrous sulfate-selenium as a catalyst. At the same time, check runs were made using copper sulfate-selenium, in order to compare digestion times. Sulfuric-salicylic acid was used in every case as a digestion medium. The digestion times shown in Table I are averages based on duplicate analyses.

While the differences in digestion times do not appear to be significant, this may be due in part to inequalities of the burners, in spite of the care used in regulating the heating. However, the efficiency is at least that of copper sulfate-selenium, and the results obtained justify the use of ferrous sulfate-selenium as a catalyst for reducing digestion time.

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# Determination of Palladium by Means of Potassium Iodide

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ALTHOUGH potassium iodide has long been used as a reagent for the determination of palladium, very little data have been published concerning suitable conditions for precipitation. Scott (2) and Bugbee (1) have stated that excess potassium iodide must be avoided, and it has been generally accepted in practice that the solution must not be boiled during precipitation. Winkler (3) has discussed the use of palladium salts for the determination of iodide in the presence of other halides. The data recorded below indicate desirable conditions for the complete precipitation of palladium iodide as well as the influence of associated precious metals on this precipitation.

## Effect of Excess Potassium Iodide

A standard palladium nitrate solution was prepared by dissolving 2.000 grams of pure palladium sponge in aqua regia and evaporating several times with nitric acid and sodium nitrate. The final residue was dissolved in 200 ml. of water and 15 ml. of nitric acid, then filtered and diluted to 1 liter. Nitric acid was used because it is associated with palladium in the wet treatment of the assay prill and regulus. When treated with dimethylglyoxime and burned as metal, 25.0 ml. of this solution yielded 50.0 mg. of palladium. A second standard solution similarly prepared yielded 25.1 mg. of palladium in 25.0 cc. of solution. A third solution yielded 25.2 mg. of palladium in 25.0 cc. of solution.

Table I describes the results obtained on treating the standard solutions with potassium iodide under varied conditions.

## Separation of Palladium and Gold

Because gold iodide redissolves in excess potassium iodide and palladium iodide only in an extremely large excess, it was decided to determine whether or not these metals might thus be separated.

Each sample of 150-ml. volume contained 25.3 mg. of palladium, 25.0 mg. of gold, and 3 ml. of concentrated nitric acid.

Preliminary experiments indicated that 40 ml. of 1 per cent potassium iodide would redissolve the gold iodide from 25.0 mg. of gold. Sample 1 was treated with 75 ml. of 1 per cent potassium iodide solution and coagulated. The precipitate was allowed to stand with occasional stirring for 30 minutes and then washed with 600 ml. of cold water. The metal recovered weighed 25.5 mg. Sample 2 was treated with 60 ml. of the iodide solution. The crystals were washed with 0.5 per cent potassium iodide solution and then with 600 ml. of cold water. The metal recovered weighed 25.7 mg. Sample 3 was treated with 80 ml. of the iodide solution and the crystals were washed with 600 ml. of cold water. The metal recovered weighed 25.5 mg. Another sample similarly treated, except that the crystals were washed with 600 ml. of hot water, yielded 25.3 mg. of metal.

Sample 4 was treated by pouring the precious metal solution into 80 ml. of hot 1 per cent potassium iodide solution. The crystals were washed with 600 ml. of hot water and the metal recovered weighed 26.3 mg.

A large number of determinations with this separation of gold from palladium produced results which were generally high. Because a reprecipitation would be necessary, the authors prefer to use existing methods for the determination of gold in the presence of palladium.

## Platinum Metals with Potassium Iodide

A solution of platinum chloride and sodium rhodium chloride made up to contain 1.2 per cent of nitric acid yielded a precipitate on warming with 1 per cent of potassium iodide solution. Precipitation was not complete.

A 1.2 per cent by weight nitric acid solution of ruthenium tetrachloride and iridium tetrachloride yielded no precipitate on warming and boiling.

## Summary

Palladium can be determined on the macro and micro scale by direct weighing as palladium iodide.

The palladium iodide can be safely boiled in the presence of an acid concentration up to about 0.8 N.

TABLE I. EFFECT OF CONDITIONS ON PRECIPITATION OF PALLADIUM BY POTASSIUM IODIDE

Sample No.	Conditions of Precipitation	Palladium— Recovered with potassium iodide		Notes
		Added Mg.	Mg.	
1	Volume made up to 125 ml.	50.0	50.0	Filtrates from 1 to 5 yielded no palladium dimethylglyoxime
2	20 ml. of 1.0% KI and	50.0	50.0	
3	2 ml. of concd. HNO <sub>3</sub>	50.0	50.1	
4	added. Temperature just below boiling for 20 min.	50.0	50.0	
5	Volume made up to 125 ml. 15 ml. of 10% KI. Mixture left standing about 15 hours	25.0	25.0	
6	Volume made up to 125 ml. 50 ml. of 10% KI. Mixture kept just below boiling for 30 min.	25.0	23.7	Filtrate treated with dimethylglyoxime yielded 1.4 mg. of palladium, a total of 25.1 mg.
7	Volume made up to 125 ml. 5 ml. of concd. HNO <sub>3</sub> and	25.0	25.1	.....
8	20 ml. of 1% KI added. Mixture kept almost boiling for 20 min.	25.0	25.1	
9	Treated like 7 and 8, except that mixture was allowed to stand for 24 hours and then boiled for 5 min.	25.0	25.0	Same volume of concd. H <sub>2</sub> SO <sub>4</sub> and HCl used and similarly treated without loss of palladium
10		25.0	24.9	
11	Treated like 7 and 8, except that boiling was continued for 30 min.	25.0	25.0	.....
12	Volume made up to 125 ml. 20 ml. of 1.0% KI and 2	25.2	25.2	Crystals of PdI <sub>2</sub> filtered by porous-bottomed porcelain filtering crucible, A2 grade, dried at 110° C. for an hour, and weighed as PdI <sub>2</sub> . PdI <sub>2</sub> can be burned to the metal, reduced in hydrogen, and cooled in carbon dioxide with much less danger of loss than with palladium dimethylglyoxime
13	ml. of concd. HNO <sub>3</sub> added. Temperature just below boiling for 20 min.	25.2	85.3 <sup>a</sup>	
			25.2	
			85.4 <sup>a</sup>	
14		50.0	50.0	
			168.1 <sup>a</sup>	
15	Each sample of spectrographically pure metal dissolved in aqua regia and evaporated three times with HCl in presence of NaCl. Iodide precipitated by 0.8 ml. of 1% KI and HNO <sub>3</sub> adjusted to about 0.8 N. Crystals filtered by 3-ml. grade A2 filtering crucible and weighed as PdI <sub>2</sub>	5.01	5.00	.....
16		6.27	6.28	.....
17		4.67	4.66	.....
18	Treated like 15 to 17, but mixture allowed to stand for 24 hours	11.35	11.36	.....
19	Treated like 15 to 17, but 8 times required amount of KI used	5.43	5.39	.....
20	Treated like 15 to 17, but 14 times required amount of KI used	6.60	6.61	.....

<sup>a</sup> Weight of palladium iodide recovered.



At least 10 times the calculated amount of potassium iodide may be added without danger of palladium loss.

Palladium iodide is much more easily burned without loss than is palladium dimethylglyoxime.

Palladium may be separated from gold by means of potassium iodide, but the results are generally high.

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# Determination of Free Sodium Cyanide and Ammonia in Brass Plating Solutions

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**T**HE free or uncombined cyanide content of a brass plating solution refers to the sodium cyanide in excess of that required to form the complex copper and zinc cyanides (2). The amount of free cyanide in the plating bath has a marked effect on the appearance and composition of the brass deposit, the cathode and anode efficiencies, the anode polarization, and the conductivity of the solution (15, 16, 19).

In general, the free cyanide in any cyanide plating solution is determined by titration with silver nitrate, using potassium iodide as indicator (2, 20). Inconsistent results are obtained, however, when this method is applied to brass plating solutions. The removal of the sodium carbonate before titration

with silver nitrate is said to overcome most of the difficulty (3, 8), although the interference of sodium carbonate may be avoided by suitably diluting the sample to be titrated (16). Pan (16) has shown that ammonium hydroxide and potassium iodide influence the value of the free cyanide, and recommends that the titration be carried out in the presence of 0.37 *N* potassium iodide indicator in order to give accurate results. However, he neglected to consider the effect of free alkali or pH, which Blum and Hogaboom (3) have pointed out makes the determination and calculation of free cyanide uncertain.

In contrast with this lack of agreement regarding the direct titration of free cyanide in brass plating solutions, the determination of cyanide in copper and zinc plating baths has been satisfactorily worked out. Thompson (21) has shown that when a copper cyanide solution is titrated with silver nitrate, a reproducible value of free cyanide—that is, the cyanide in excess of that required to form the compound  $\text{Na}_2\text{Cu}(\text{CN})_3$ —is obtained when 0.5 to 1.0 gram of potassium iodide per 100 ml. of solution is used as an indicator. If the same method of titration for free cyanide is applied to a zinc cyanide solution, inconsistent results are obtained, owing to the effect of variations in total alkalinity or pH on the equilibrium between sodium zincate and sodium zinc cyanide. However, an accurate and reproducible value of the total cyanide may be obtained by adding an excess of sodium hydroxide to the solution and then titrating with silver nitrate (4). When this procedure for the determination of the total cyanide in a zinc plating solution is applied to a brass plating solution, the cyanide in the zinc complex plus the free cyanide should be obtained. One object of this investigation was to evaluate this method.

### Evolution Method for Total Cyanide and Ammonia

Coates (7) has recommended an evolution method for determining the total cyanide in a brass plating solution, by means of which the uncombined cyanide can readily be calculated. Wick (22) has determined the total cyanide in a cyanide silver plating solution by distilling with sulfuric acid. It was thought desirable to investigate this evolution method for the determination of total cyanide, with the idea of making it as simple as possible in operation and detail, so that it could be used as a routine test.

Page and Carlson (14) have recently decomposed sodium cyanide quantitatively by the distillation of hydrocyanic acid from sulfuric acid solutions, and Morris and Lilly (13) have made further studies of this method.

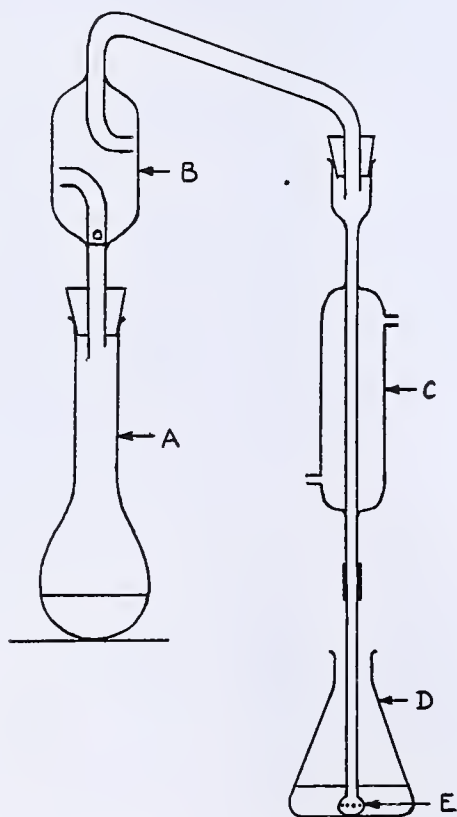


FIGURE 1. DISTILLATION APPARATUS

- A. 300-ml. short-necked Kjeldahl flask
- B. Connecting bulb, Southern Oil Co. model
- C. Condenser, 50 cm. long
- D. 250-ml. Erlenmeyer flask
- E. Gas distributor. Miller (12) has shown that this device ensures better absorption by breaking up the large bubbles of gas.



Using the apparatus shown in Figure 1, tests were made with technical zinc cyanide. Dilute sulfuric acid was added to zinc cyanide suspended in water and the hydrocyanic acid distilled into a sodium hydroxide solution. The sodium cyanide formed was titrated with standard silver nitrate. The average of four distillations gave 99.88 per cent recovery of the cyanide content, as compared with the results obtained by titration of the total cyanide with silver nitrate in the presence of potassium iodide and sodium hydroxide.

In a similar manner, it was found that by distilling cuprous cyanide with a mixture of sulfuric and hydrochloric acids (1), or with hydrochloric acid alone, an average recovery of 99.73 per cent of the theoretical cyanide content of the cuprous cyanide was obtained.

An old brass plating bath may contain iron as ferrocyanide, and the cyanide in this ferrocyanide will be included in the total cyanide as determined by the evolution method. Knowing the iron content of the plating solution, the sodium cyanide equivalent to the ferrocyanide may be calculated, and accounted for in the calculation of the free cyanide. However, in a given plating bath, the amount of ferrocyanide will not change appreciably, and for routine control work the correction will remain substantially constant and may be neglected.

There is some disagreement in the literature as to the formula of the complex zinc cyanide present in a brass plating solution. Most text books (5) give  $\text{Na}_2\text{Zn}(\text{CN})_4$ . Pan (18) concluded that the compound has the formula  $\text{NaZn}(\text{CN})_3$ , but there was considerable criticism of his work. The authors have chosen the  $\text{Na}_2\text{Zn}(\text{CN})_4$  formula in calculating the free cyanide from the results obtained by the evolution and titration methods.

Ammonium hydroxide is commonly added in very small quantities to a fresh brass plating bath at the time of preparation in order to improve its initial operation (6). One pint of concentrated ammonium hydroxide per 100 gallons of solution is usually recommended. It is believed that a small quantity of ammonia forms in an old plating bath as a result of the decomposition of free cyanide (23).

More recently Pan (17) has shown that the presence of ammonia in somewhat larger quantities—i. e., 1 to 7 ml. per liter of solution—markedly affects the deposits that may be obtained from a brass plating bath. While the amounts of ammonia recommended by Pan are not known to be employed commercially, it would be interesting to know the ammonia concentration of an old plating bath. Furthermore, if a convenient method for the control of the ammonia concentration were available, some of the advantages recommended by Pan might be realized in practice. An evolution method to determine ammonia in cyanide solutions was therefore investigated.

Meeker and Wagner (11) have suggested the use of a boric acid solution instead of a standard acid solution for the absorption of ammonia. Using this modification of the standard evolution method, four distillations using c. p. ammonium chloride gave an average recovery of 99.74 per cent of the calculated amount of ammonia. This method offers the advantage of requiring only one standard solution.

**PROCEDURE FOR TOTAL CYANIDE.** The apparatus was assembled as shown in Figure 1. Five milliliters of brass solution containing ammonia equivalent to 0.22 gram of ammonium chloride were transferred to the Kjeldahl flask, and then 50 ml. of water and a few pieces of porous plate were added. Seventy milliliters of 1.5 per cent sodium hydroxide were added to the Erlenmeyer flask receiver, 10 ml. of concentrated hydrochloric acid, diluted to 100 ml., were poured into the distillation flask, and the connecting bulb was immediately replaced. The solution was then distilled for 45 minutes, during which time about half the contents of the flask distilled over. After the distillation, the condenser and gas distributor were rinsed with distilled

water, running the washings into the receiver. The sodium cyanide in the receiver was titrated with 0.100 N silver nitrate solution in the presence of 6 ml. of 6 N ammonium hydroxide containing 3.3 per cent of potassium iodide. The end point was obtained at the appearance of a bluish opalescence (9). The solution remaining in the distillation flask was used for the determination of ammonia. Cyanide and ammonia were thus determined on the same sample.

**PROCEDURE FOR AMMONIA.** After cooling the flask to room temperature, 70 ml. of 10 per cent sodium hydroxide solution were added to the Kjeldahl flask and the ammonia was distilled into an Erlenmeyer flask containing 80 ml. of 4 per cent boric acid. The receiver was kept on an ice bath, and the distillation carried out for 45 minutes, during which time about half of the volume of the solution distilled over. After rinsing the condenser and gas distributor, the ammonia in the receiver was titrated with standard 0.1 N hydrochloric acid, using 2 drops of methyl red as indicator.

**DISCUSSION OF RESULTS.** A typical brass plating solution, similar to that used in practice, was made up with the following composition:

Brass Plating Solution No. 1		
	G./l.	
Cu	18.63	
CuCN	26.25	C. P.
Zn	4.59	
Zn(CN) <sub>2</sub>	8.25	Tech. 92.5% of the theoretical cyanide content by analysis
NaCN	43.50	C. P. 96.6% NaCN by analysis
Na <sub>2</sub> CO <sub>3</sub>	30.00	C. P.

By calculation on the basis of direct analyses of the above reagents, 5 ml. of this solution contain 0.3140 gram of sodium cyanide (including the sodium cyanide equivalent to the cyanide in the cuprous cyanide and zinc cyanide).

Table I gives the results obtained on distilling 5 ml. of brass solution No. 1 as given in the procedure. An average of 99.1 per cent of the total cyanide in the plating solution was recovered. It is interesting to note that after the solution had stood for 2 months in the laboratory, about 1.5 per cent of the total cyanide had decomposed and was recovered as ammonia on distilling with sodium hydroxide.

The uncombined sodium cyanide in the brass plating solution was calculated in the following manner: The copper and zinc contents of the solution multiplied by 2.312 and 2.998, respectively, gave the sodium cyanide equivalents in the cyanide complexes  $\text{Na}_2\text{Cu}(\text{CN})_3$  and  $\text{Na}_2\text{Zn}(\text{CN})_4$ . The sum of these equivalents subtracted from the total cyanide content gave the free or uncombined sodium cyanide.

As a check of the previous work, a second brass plating solution was prepared having the following composition:

Brass Plating Solution No. 2		
	G./l.	
Cu	18.63	
CuCN	26.25	C. P.
Zn	4.59	
ZnO	5.72	C. P.
NaCN	50.37	96.4% NaCN by analysis
Na <sub>2</sub> CO <sub>3</sub>	30.00	C. P.

Five milliliters of this solution contain 0.3147 gram of total sodium cyanide by calculation, including the sodium cyanide equivalent to the cyanide in the cuprous cyanide.

Table I also gives the results obtained in analyzing this second solution for both total cyanide and ammonia by the evolution methods previously described. The average recovery of total sodium cyanide, 99.09 per cent, is about the same as that with the first brass plating solution. The slightly low values obtained on the total cyanide recovery are probably due to hydrolysis of the sodium cyanide to ammonium formate during the distillation (10). This may account for the fact that the recovery of the total cyanide is about 1 per cent low and the ammonia recovery is about 1 per cent high.



TABLE I. DETERMINATION OF TOTAL CYANIDE AND AMMONIA IN BRASS PLATING SOLUTIONS BY THE EVOLUTION METHOD  
(5 ml. of brass plating solution used in all distillations. Weight of "NaCN present" is the sum of sodium cyanide plus sodium cyanide equivalents of copper cyanide and zinc cyanide.)

Brass Solution No.	Condition	Total NaCN Present	NaCN Recovered		Free NaCN Present	Free NaCN Found		NH <sub>3</sub> Added (as NH <sub>4</sub> Cl)	NH <sub>3</sub> Recovered	
		G./5 ml. solution	Gram	%	G./l.	G./l.	%	G./5 ml. solution	Gram	%
1	Fresh	0.3140	0.3110	99.06	..	..	...	None	.....	...
		0.3140	0.3112	99.13	..	..	...	None	.....	...
		Av.	0.3111	99.09	6.98	6.40	91.68	None	.....	...
1	After standing two months	0.3140	0.3063	97.54	..	..	...	0.07180	0.07305	101.7
		(Originally)			..	..	...			
		0.3140	0.3067	97.68	..	..	...	0.07099	0.07266	102.3
2	Fresh	Av.	0.3065	97.61	..	..	...	0.07140	0.07286	102.0
		0.3147	0.3115	98.97	..	..	...	0.07193	0.07247	100.9
		0.3147	0.3119	99.10	..	..	...	0.07076	0.07147	101.0
		Av.	0.3117	99.04	6.08	5.48	90.14	0.07135	0.07197	101.0

### Titration Method for Free Cyanide

Five milliliters of brass plating solution No. 2 were titrated with 0.1 *N* silver nitrate solution in the presence of various amounts of potassium iodide and sodium hydroxide as recorded in Figure 2. The horizontal dotted line shows the value of 19.87 grams per liter of sodium cyanide, which is that calculated on the basis of the free cyanide plus the sodium cyanide equivalent to the sodium zinc cyanide, Na<sub>2</sub>Zn(CN)<sub>4</sub>. [The zinc content of the solution multiplied by 2.998 gives the sodium cyanide equivalent to the Na<sub>2</sub>Zn(CN)<sub>4</sub>.] Using 100 ml. as the total volume at the end of the titration with silver nitrate, in the presence of from 2.0 to 4.0 grams of sodium hydroxide and 1.5 to 3.0 grams of potassium iodide, the above calculated value of sodium cyanide is obtained.

These results indicate that the cyanide content of the sodium copper cyanide, Na<sub>2</sub>Cu(CN)<sub>3</sub>, is not titrated under these conditions. It is possible, therefore, to determine the free cyanide by direct titration with silver nitrate in the presence of potassium iodide and sodium hydroxide, provided the zinc content of the plating bath is known.

The presence of ammonia in cyanide plating solutions gives higher values of free sodium cyanide when determined by titration with silver nitrate (16, 21). A similar effect of ammonia has been observed in titrating the cyanide present as free sodium cyanide and sodium zinc cyanide in a brass plating solution using silver nitrate, sodium hydroxide, and potassium iodide as recommended above. Since only 5 ml. of the plating solution are used in the titration, the amount of ammonia normally present in a brass plating bath is not sufficient to affect the accuracy of the titration. Even an

excessively large amount of sodium carbonate (90 grams per liter) did not interfere with the sharpness of the end point or the accuracy of the method. The dilution of the sample being titrated was found to have only a slight effect on the value of the sodium cyanide. The effects of ammonia, sodium carbonate, and dilution on this method of titration are given in Table II.

TABLE II. TITRATIONS OF BRASS PLATING SOLUTION NO. 2  
(Sample for titration, 5 ml. Volume at end of titration, 100 ml. Sodium hydroxide used, 4.0 grams. Potassium iodide used, 2.0 grams)

Effect of Na <sub>2</sub> CO <sub>3</sub>	NaCN <sup>a</sup> found	Effect of Dilution		Effect of NH <sub>4</sub> OH <sup>b</sup>	NaCN found
		Volume at end of titration	NaCN found		
G./l.	G./l.	ml.	G./l.	Cc./5 ml. solution	G./l.
30	20.10	75	20.00	0.2	20.10
60	20.10	100	20.10	1.0	20.50
90	20.10	150	20.20		

<sup>a</sup> Calculated amount of free cyanide plus NaCN equivalent to Na<sub>2</sub>Zn(CN)<sub>4</sub> equals 19.87 grams per liter.

<sup>b</sup> 10 ml. aqua ammonia per liter of brass plating solution equals 0.05 ml. per 5-ml. sample.

**TITRATION PROCEDURE FOR DETERMINING FREE CYANIDE.** Five milliliters of the brass plating solution were transferred to a 250-ml. Erlenmeyer flask and 20 ml. of 20 per cent sodium hydroxide solution, 20 ml. of 10 per cent potassium iodide solution, and 40 ml. of water were added. The solution was then titrated with 0.1 *N* silver nitrate solution to the appearance of a bluish opalescence.

The free sodium cyanide in the brass plating solution may be calculated as follows: The number of milliliters of silver nitrate used in the titration multiplied by 1.960 equals the number of grams per liter of sodium cyanide on the basis of the free cyanide, plus the sodium cyanide equivalent to the sodium zinc cyanide, Na<sub>2</sub>Zn(CN)<sub>4</sub>. The latter may be found by multiplying the zinc content of the bath (expressed in grams per liter) by 2.998. The free sodium cyanide may be obtained by difference.

### Summary

The total cyanide and ammonia content of a brass plating bath may be determined by evolution methods. The error is about 1 per cent. The free cyanide may be calculated, knowing the copper and zinc content, with an error of approximately 10 per cent. The free cyanide may also be determined by a titration method in which both the free cyanide and sodium cyanide equivalents of the sodium zinc cyanide, Na<sub>2</sub>Zn(CN)<sub>4</sub>, are titrated. In this case the free cyanide may be calculated knowing the zinc content. The error by the titration method is about 2 per cent.

In the evolution method, the accuracy of the determination of free cyanide depends upon the accuracy of the zinc and copper determination. The accuracy obtained by the titration method depends upon the accuracy of the zinc determination. However, since the cyanide in the brass plating solution must be destroyed before the ammonia may be determined, the analyses for free cyanide and ammonia by the evolution method may be conveniently carried out together.

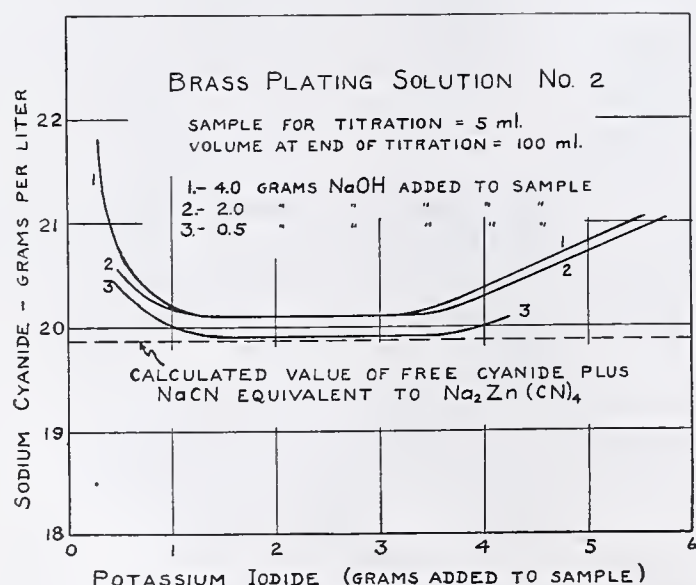


FIGURE 2. DETERMINATION OF CYANIDE IN BRASS PLATING SOLUTION



The free cyanide may be determined by either the evolution or the titration method with sufficient ease and accuracy for practical routine control purposes.

### Acknowledgment

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# Determination of Dissolved Oxygen

## Rideal Stewart and Alsterberg Modifications of the Winkler Method

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AMONG the many modifications of the Winkler method advocated for the determination of dissolved oxygen in the presence of nitrite, probably the most widely used is the Rideal Stewart method. Because it has been recognized for some time that in the presence of organic matter this modification gives low results, other modifications have been proposed. Noll (5) proposed the use of urea for the destruction of nitrites but, as Alsterberg (1) has pointed out, its use requires a long period of contact (approximately 24 hours) and is, therefore, impracticable. Alsterberg substituted sodium azide for urea and found that the destruction of nitrite could be accomplished in a few minutes. Ohle (6), summarizing methods used for the determination of dissolved oxygen in the presence of nitrite, did not consider the azide method important. However, as pointed out by Brandt (3), this modification has been used extensively in Germany on river studies.

In the course of previous work (4) on the determination of the solubility of oxygen in sewage, a number of modifications of the Winkler method were used. This work has since been extended to include the azide modification. The results obtained were so promising that it was decided to make a comparative study of the sodium azide and Rideal Stewart modifications during the course of a survey of the Scioto River. The results obtained by these two methods on samples from this polluted stream are given in the present paper.

### Experimental Methods

In this study the samples of water were collected from regular sampling stations distributed along the Scioto River from 3 to 115 miles from Columbus, Ohio. The samples of water that were to be used for comparative dissolved oxygen determinations by the two methods were obtained simultaneously in two standard 300-ml. bottles contained in one standard sampling apparatus for collecting samples for dissolved

oxygen determinations. All samples were tightly stoppered and immediately transported by automobile to a central laboratory at Chillicothe, Ohio, for analysis upon arrival. The maximum elapsed time between collection and analysis of any of these samples was 3 hours. All samples from the majority of sampling stations were analyzed within 2 hours after they were collected.

The Rideal Stewart (permanganate) procedure (2) was used on one series of samples. On the series of duplicate samples the sodium azide procedure was used to destroy the nitrite contained therein. However, the sodium azide procedure of Brandt (3) was reversed—that is, the nitrite was destroyed in acid solution before the Winkler procedure and consequent liberation of iodine, in order that the free iodine might not react with any organic matter present during the time interval allowed for nitrite destruction and thus tend to give low results. The following procedure was found to be entirely satisfactory even though the nitrite concentration might be as high as 4.0 p. p. m.

To the sample of water in a standard 300-ml. bottle, 0.7 ml. of concentrated sulfuric acid is added, followed by 0.8 ml. of a 2.0 per cent aqueous solution of sodium azide. The bottle is stoppered, the contents are mixed by shaking, and the bottle is allowed to stand for 10 minutes. One milliliter of manganous sulfate solution and 3.0 ml. of alkaline potassium iodide solution are next added and the sample is shaken for 20 seconds. Following this the precipitate is allowed to settle and the sample is acidified with 2.0 ml. of concentrated sulfuric acid. The liberated iodine on a volume of solution equivalent to 200 ml. of the original sample is titrated immediately with 0.025 *N* sodium thiosulfate, using starch indicator.

The 10-minute interval of standing after mixing the sodium azide solution with the acidified sample is necessary for the completion of the azide nitrite reaction and destruction of the nitrite.



TABLE I. BIOCHEMICAL OXYGEN DEMAND AND NITRITE CONTENT  
(Scioto River water samples used in comparative study of dissolved oxygen methods)

Sampling Point	Miles from Columbus	5-Day B. O. D. <sup>a</sup> P. p. m.	Nitrite Nitrogen Range Min. Max. P. p. m. P. p. m.	
			P. p. m.	P. p. m.
Columbus	3	2.63	0.0	0.48
Shadeville	13	12.39	Tr.	1.25
Commercial Point	17	7.12	0.04	0.75
South Bloomfield	23	5.47	0.07	1.0
Red Bridge	30	4.26	0.05	0.8
Circleville	33	3.47	0.05	0.5
Penn. R. R. Bridge	35	6.04	Tr.	0.5
Kellenberger	46	4.88	0.05	0.5
Chillicothe	61	4.85	0.0	0.15
Kilgore	67	4.45	0.0	0.15
Highy	76	4.31	0.0	0.05
Waverly	92	3.64	0.0	0.05
Lucasville	115	3.49	0.0	0.05
Paint Creek <sup>b</sup>		6.41	Tr.	0.35

<sup>a</sup> Mean for May, June, and July.  
<sup>b</sup> This tributary discharges into the Scioto River below Chillicothe, Ohio.

TABLE II. COMPARISON OF DISSOLVED OXYGEN RESULTS ON 411 SCIOTO RIVER SAMPLES  
(Sodium azide and Rideal Stewart modifications of the Winkler method)

Sampling Station	No. of Samples	Mean Dissolved Oxygen		Deviation P. p. m.
		Sodium azide modification P. p. m.	Rideal Stewart modification P. p. m.	
Columbus	38	7.50	7.26	0.24
Shadeville	39	3.16 <sup>a</sup>	2.94 <sup>a</sup>	0.22
Commercial Point	38	3.11 <sup>b</sup>	2.91 <sup>b</sup>	0.20
South Bloomfield	42	2.42	2.23	0.19
Red Bridge	38	3.47	3.34	0.13
Circleville	38	4.53	4.34	0.19
Penn. R. R. Bridge	38	4.44	4.10	0.34
Kellenberger	23	4.51	4.23	0.27
Chillicothe	13	6.54	6.20	0.34
Kilgore	10	6.36	6.10	0.26
Highy	13	6.44	6.16	0.28
Waverly	10	7.32	7.04	0.28
Lucasville	10	7.60	7.37	0.27
Paint Creek	22	7.38	7.10	0.28
Miscellaneous	39	6.93	6.63	0.30

<sup>a</sup> 13 samples were 0.0 by each method and were not included in this average.  
<sup>b</sup> 6 samples were 0.0 by each method and were not included in this average.

Analytical Results

Four hundred and eleven pairs of duplicate samples of water from the Scioto River have been analyzed by the two methods described. Table I gives the mean 5-day biochemi-

cal oxygen demand and the nitrite range encountered at the sampling points during the period of investigation. These data show that the mean 5-day B. O. D. ranged from 2.63 p. p. m. at Columbus above the sewer outlets to 12.39 p. p. m. at Shadeville, the point of maximum pollution. Each figure represents the mean of the results from 40 or more individual samples collected at 2-day intervals during this period. The nitrite nitrogen range obtained during this period is wide, and it is apparent that some method for destroying the nitrite must be used before the Winkler method for dissolved oxygen is applicable.

The dissolved oxygen results obtained by both methods on all the samples arranged according to sampling stations are presented in Table II. These data indicate that the sodium azide modification gives slightly higher average results than the Rideal Stewart modification. The actual mean differences in dissolved oxygen are not great at Shadeville, Commercial Point, and South Bloomfield where the dissolved oxygen values are low and the B. O. D. values are highest. The percentage deviations are greatest, however, at these points. The mean difference between the sodium azide results and the Rideal Stewart results increased to about 0.3 p. p. m. at some of the lower stations where the dissolved oxygen content is higher. These results do not suggest any correlation between the mean B. O. D. at a station and the mean deviation of the dissolved oxygen results obtained by these methods.

To determine whether the dissolved oxygen content had any influence upon the mean deviations between the results by these methods, all the results were arranged in groups on

TABLE III. COMPARISON OF DISSOLVED OXYGEN RESULTS ON 411 SCIOTO RIVER SAMPLES

(Sodium azide and Rideal Stewart modifications of the Winkler method. Results arranged in groups on basis of D. O. content found by the azide modification)

Dissolved Oxygen Range of Group P. p. m.	No. of Samples	Mean Dissolved Oxygen		Mean Deviation P. p. m.
		Azide modification P. p. m.	R-S modification P. p. m.	
0.0	19	0.0	0.0	0.0
0.27 to 0.99	6	0.53	0.46	0.07
1.0 to 2.99	70	2.17	2.03	0.14
3.0 to 4.99	140	4.15	3.85	0.30
5.0 to 6.99	98	6.03	5.70	0.33
Over 7.0	78	8.42	8.11	0.31

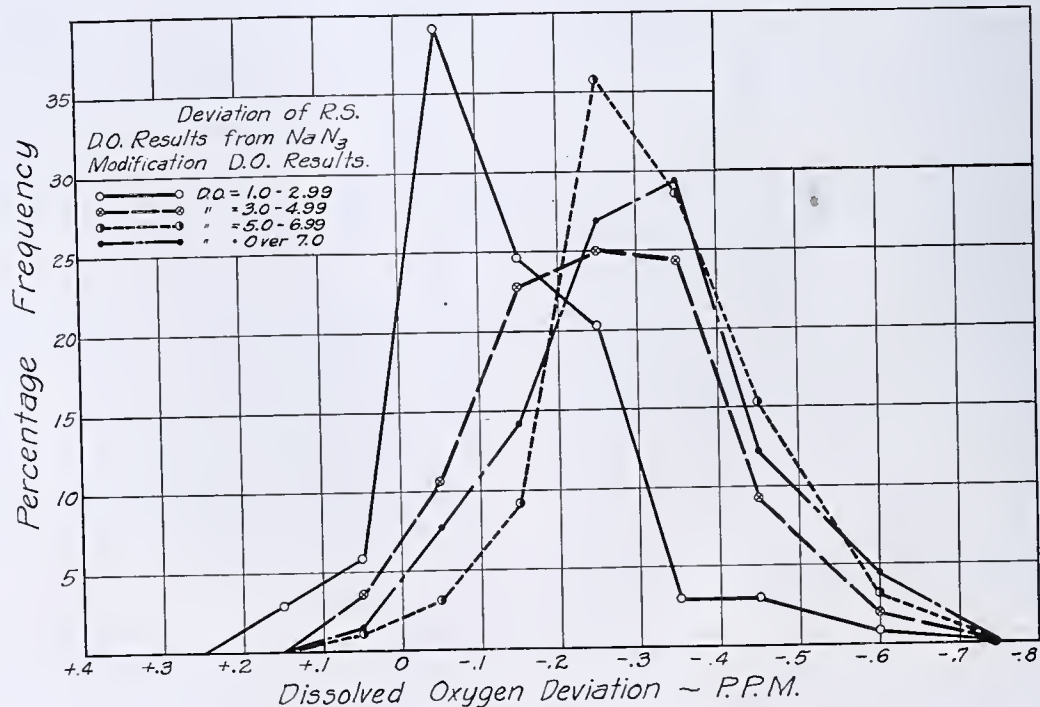


FIGURE 1. DEVIATION FREQUENCY



TABLE IV. DEVIATION FREQUENCY BETWEEN DISSOLVED OXYGEN RESULTS

(Sodium azide and Rideal Stewart modifications arranged in groups according to dissolved oxygen content)

Range of D. O. Content in Groups	Deviation Frequency of Rideal Stewart Results from Sodium Azide Modification Results in Stated Deviation Groups										
	+0.31 and higher	+0.30 to +0.21	+0.20 to +0.11	+0.10 to 0.00	0.00 to -0.10	-0.11 to -0.20	-0.21 to -0.30	-0.31 to -0.40	-0.41 to -0.50	-0.51 to -0.75	Under -0.76
0.27-0.99	..	..	..	16.67	50.00	33.33	..	..	..	1.45	..
1.00-2.99	..	..	2.90	5.80	39.13	24.63	20.29	2.90	2.90	..	..
3.00-4.99	0.71	..	..	3.57	10.71	22.86	25.00	24.29	9.29	3.57	..
5.00-6.99	..	..	..	1.02	3.06	9.18	35.71	28.57	15.31	6.12	1.02
Over 7.00	..	1.28	..	1.28	7.69	14.10	26.92	29.49	10.26	8.97	..

the basis of the dissolved oxygen found by the sodium azide method as shown in Table III. The results of this arrangement seem to suggest that the quantity of oxygen present affects the mean deviation between the results obtained by these methods. When all the results are included the mean deviations tend to increase with the dissolved oxygen of the samples at least until an oxygen content of 7.0 p. p. m. is reached.

The frequency at which deviations of various magnitudes between the results by these methods occur for the groups of samples at each dissolved oxygen range given in Table III has been determined and is presented in Table IV. These data indicate that in the great majority of samples the oxygen content found by the azide modification will be higher than that found by the Rideal Stewart modification. With samples containing more than 1.0 p. p. m. of oxygen higher results were obtained with the Rideal Stewart modification on only about 5.0 per cent of the samples. These data indicate that the frequency of greater negative deviations by the Rideal Stewart method tends to increase as the dissolved oxygen content of the samples increases. This is illustrated by the plot of the deviation frequency shown in Figure 1.

### Discussion

The results obtained by the two methods check surprisingly well on the Scioto River. As it has been shown (7, 8) that the Rideal Stewart modification tends to give low results in the presence of stale sewage and other forms of organic matter, it seems reasonable to ascribe the predominant negative deviations obtained by this modification to adsorption of oxygen by the organic matter during the permanganate treatment.

The sodium azide modification is very effective in nitrite destruction. The paucity of times that the starch-iodine color returns at the end point of the titration is evidence of this effectiveness. Of the 411 determinations made by this method, a return of color after titration was noted only once. In the presence of high nitrite concentration (4.0 p. p. m. or more) the manganous hydroxide floc tends to rise in the bottle. However, if the bottle is shaken the second time the nitrogen will be disengaged and the floc will settle satisfactorily. The azide method is one operation shorter than the Rideal Stewart method in that it is unnecessary to destroy the excess azide, whereas with the Rideal Stewart method it is necessary to destroy the excess permanganate with oxalate. This step often causes difficulties because of errors introduced by starting the Winkler procedure before all color has disappeared or adding an excess of oxalate.

As the azide method has advantages in technique, is effective in destroying nitrite, and seems less affected than the permanganate treatment by organic matter it would seem very desirable in dissolved oxygen studies.<sup>1</sup> The results obtained in this study suggest that the method can be success-

<sup>1</sup> Additional data have been obtained upon the use of these two methods in determining the dissolved oxygen in sewage where nitrites and larger quantities of organic matter are encountered and in water samples containing either but not both of these interfering substances. In the interest of brevity these observations are not presented at this time.

fully applied to the determination of the dissolved oxygen content of sewage-polluted streams where nitrite is encountered. In sewages where the greatest organic matter interference occurs with the straight Winkler procedure, the azide procedure followed by the short Winkler (8) procedure is suggested. Additional study of the method seems desirable in connection with biochemical oxygen demand studies where nitrite is produced during the incubation period.

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RECEIVED September 12, 1938. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 96th Meeting of the American Chemical Society, Milwaukee, Wis., September 5 to 9, 1938.

## Determination of Free Sulfur in Fertilizers

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THE method described by the author (1) for determining free sulfur in Mexican sulfur ores has been found satisfactory with slight modifications for determining free sulfur in fertilizer. It is simple, easily manipulated, and gives results sufficiently accurate for all practical purposes.

Weigh 2 grams of sample into a 250-cc. beaker, add 75 to 100 cc. of dilute hydrochloric acid (1 to 1), and boil for 10 to 15 minutes. Filter through a Gooch crucible while hot, and wash thoroughly with hot water and finally twice with alcohol.

This treatment eliminates all the soluble salts which would interfere with the determination. Dry for at least 1 hour at 100° C., cool, and weigh. Extract the sulfur with carbon disulfide, dry again, cool, and weigh. The loss represents free sulfur.

As the Pierre method for the determination of acidity and basicity of fertilizer mixtures fails to allow for the presence of elemental sulfur, this method may be used to give a correction. An equivalent acidity of 100 pounds (45 kg.) of calcium carbonate is allowed for each 32 pounds (14.4 kg.) of elemental sulfur found in the fertilizer.

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## Microchemical Laboratory of the Abbott Laboratories

E. F. SHELBERG, Abbott Laboratories, North Chicago, Ill.

**I**N THE year 1910 Fritz Pregl, finding it necessary to analyze minute quantities of biochemical substances, developed a system of milligram analysis which is the basis of modern microchemical technique. Since this time, industrial and research chemists have discovered to an ever-increasing extent the value of a microchemical laboratory, and in 1934 Abbott Laboratories decided to install a microchemical division.

Prior to 1934 numerous samples were being analyzed for both the research and manufacturing departments and there were times when the large volume of analytical work could not be handled with sufficient promptness. This was especially true when it became necessary to analyze a series of samples using macromethods such as the Dumas, the Kjeldahl, or the carbon and hydrogen. Not only did these analyses require large samples, but the determinations were also lengthy, and in many instances finished products could have been made before it was possible to analyze the intermediates. Microchemical methods, however, brought about more efficient service for both the research and the manufacturing departments.

The first microchemical laboratory was equipped primarily for Dumas, Kjeldahl, and carbon and hydrogen determinations. This laboratory was not air-conditioned, and there was no system to control the humidity. A Kuhlmann micro-

balance was installed on a very rigid support which, nevertheless, allowed the balance to vibrate to a certain extent.

The Research Building (I) erected during 1937, includes the new microchemical laboratory. The floor plans show its location (L. M.) on the second floor. The advice of chemists and chemical engineers both in universities and in industry was sought and utilized in planning its construction.

### Rooms and Furnishings

The walls of the laboratory are of a cream-colored, mat-glaze terra cotta. Excellent light is furnished from overhead lighting fixtures of a semiindirect type. Light can also be obtained through a large glass-brick window.

The laboratory consists of a large room for analyses and a smaller room for weighings. Both rooms are completely air-conditioned; the air is washed and then passes through a filter of glass wool impregnated with oil, before it enters the room through an "Anemostat" in the center of the ceiling (not shown in picture) that distributes the air evenly without creating drafts. The air-conditioning equipment is adequate to care for more than twice the space now used.

After experimenting to decide the most desirable temperature and humidity, it was found that a temperature of from 73° to 75° F. and a humidity of 50 per cent were satisfactory, and these are maintained in the laboratory. A humidity in



RESEARCH BUILDING, ABBOTT LABORATORIES



excess of 50 per cent is less satisfactory because it sometimes causes the microbalance to stick. A recording instrument registers the temperature and humidity and furnishes a weekly graph of both. The operation of the hood in the microlaboratory does not appreciably change the temperature or humidity.

The laboratory furniture is made of steel, lead-coated with aluminum finish; the desk tops are a black asbestos-cement-



POTH CARBON DIOXIDE GENERATOR

asphalt composition. Numerous drawers and cupboards are provided, and, as they are installed in units, they can be changed at any time. The cupboards are either attached to the wall or rest upon especially made units containing drawers, and are large enough to store the reagents and much of the equipment. The laboratory tables are liberally fitted with facilities for gas, electricity, vacuum, compressed air, and water (tap and distilled). All water taps are provided with drains.

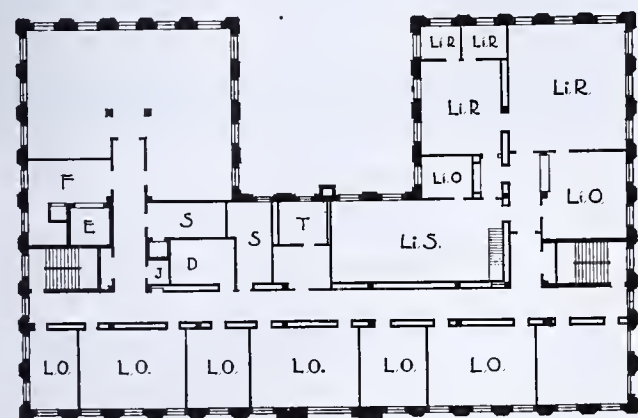
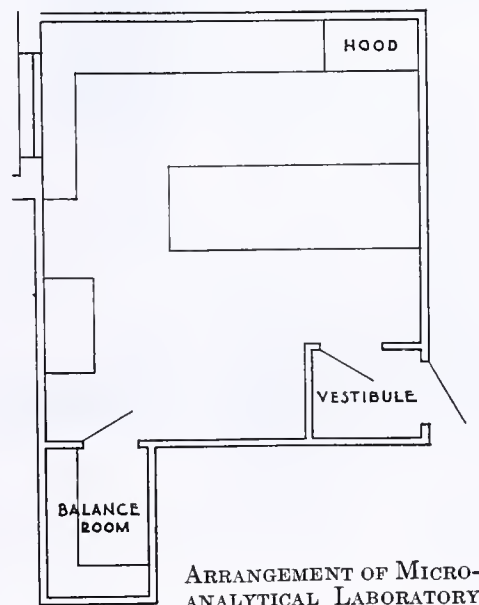
It has been found that the large dimensions of the room aid the analyst's operations by providing ample space so that certain apparatus can be set up permanently.

The balance room is of rectangular shape, and houses three balance cases which conveniently house the four balances used, and, like the rest of the furniture, are made of steel with aluminum finish. The cases are 30 inches high and 18 inches deep; two are 30 inches wide and one is 36 inches wide.

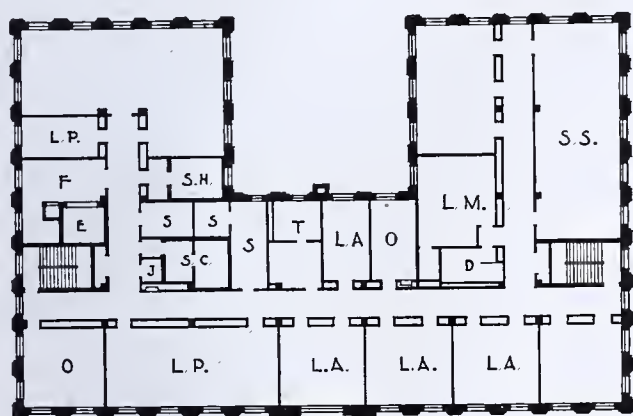
They are attached to the wall and are separate from the tables on which the balances are mounted. Lighting is obtained from movable lights that slide on a rail directly over the balance cases.

### Equipment

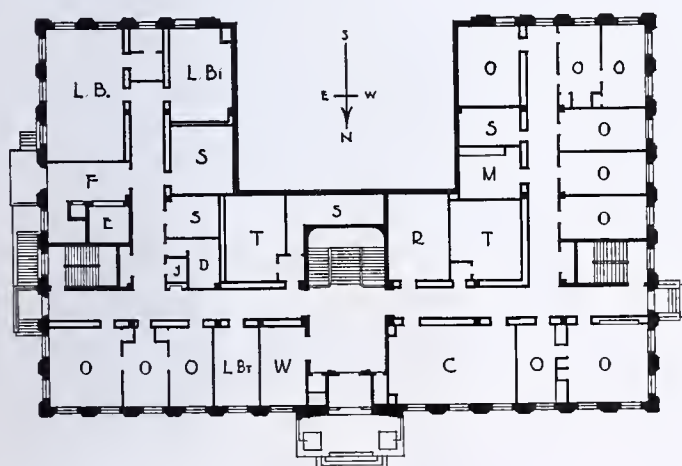
Samples requiring the same type of analysis are encountered so frequently that much of the equipment is set up perma-



THIRD FLOOR



SECOND FLOOR



FIRST FLOOR

### FLOOR PLANS OF RESEARCH BUILDING

C.	Conference room	Li.	Library
D.	Dark rooms	Li.O.	Office
E.	Elevator	Li.R.	Reading rooms
F.	Freight receiving	Li.S.	Stack room
J.	Janitor	M.	Medical first aid
L.	Laboratories	O.	Offices
L.A.	Analytical	R.	Rest room
L.B.	Bacteriological	S.	Storage
L.Bt.	Biochemical	S.C.	Cold room
L.Bt.	Botanical	S.H.	Warm room
L.M.	Microanalytical	S.S.	Sample storage
L.O.	Organic	T.	Toilets
L.P.	Pharmaceutical	W.	Reception room



nently. The Kjeldahl apparatus, for example, is used repeatedly. The Parnas-Wagner modification with an improved method of withdrawing the excess liquid from within the vacuum jacket is used for Kjeldahl distillations. Instead of waiting for the water in the steam-generating flask to cool of its own accord, cold distilled water is added quickly from a separate inlet connected to the flask. This not only saves time, but it also keeps the steam-generating flask filled with the proper amount of water.

A special rack within the large hood has been provided for Kjeldahl digestions. This has a fume duct, cylindrical in shape and mounted horizontally, from which fumes are removed by a separate fan. There are openings in the bottom of this fume duct into which the necks of the Kjeldahl flasks are inserted. Microburners are used for the digestions. The digestion of a 2- to 5-mg. sample is made with 1 cc. of fuming sulfuric acid and a small amount of selenium. Thirty per cent hydrogen peroxide is added during the digestion to aid the destruction of the compound.

In many cases nitrogen must be determined by the Dumas method. An electric furnace is used to heat the



MICROCHEMICAL LABORATORY

combustion tube, but the sample is burned with a Bunsen burner.

A Poth generator (6) is used to furnish the carbon dioxide. It is more convenient and requires less space than a series of Kipp generators and produces pure carbon dioxide at all times. Also, refilling is seldom necessary.

The top and side arm of this Poth generator are not sealed off after filling, as is usually done. Instead, the apparatus has ground-glass stoppers sealed with Kroenig cement. A bent acid-delivery tube has also been found to be advantageous, as it prevents lag in carbon dioxide evolution. When the acid-delivery tube is not bent, crystals form at the surface of the liquid around the tube. If this formation is allowed to continue until it covers a large area, there is a lag in the carbon dioxide evolution due to the fact that it takes some time for the acid to come into contact with the bicarbonate solution.

Standard micro equipment is used for carbon and hydrogen determinations, and like the Kjeldahl and Dumas apparatus is never dismantled. The laboratory is equipped with many other types of apparatus for standard microanalyses, including the following: halogens, sulfur, acetyl, methoxyl, and molecular weights. Melting points are taken on the Kofler microscopic hot stage. Qualitative analyses and spot tests (2, 3) can be made. Not only are organic compounds analyzed, but occasionally inorganic compounds are also analyzed by micromethods.

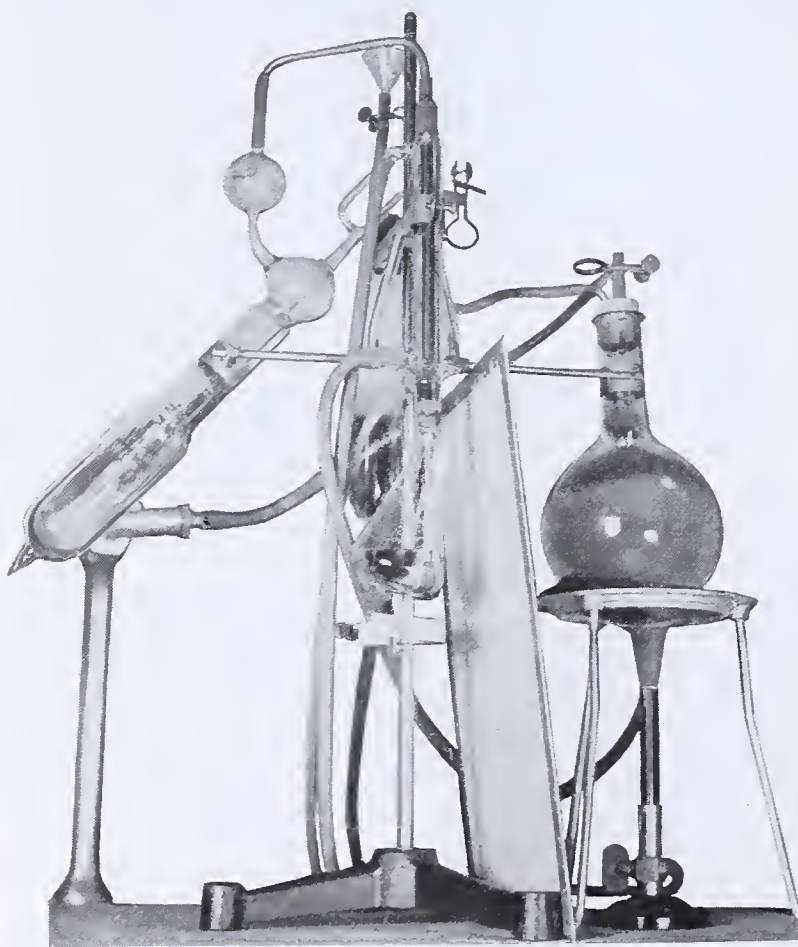
Four balances are used: a micro-Kuhlmann, a micro-Bunge, a semimicro-Christian Becker, and a Sartorius preliminary balance. The two microbalances and the semimicro-balance are mounted on hand-ball suspensions (4, 5), which are very efficient in reducing vibration to a minimum and in ensuring a constant zero point.

A hood is conveniently located next to the sink and is equipped with a safety light and a safety-glass window. On one side in the hood there is a reagent cupboard with glass doors; on the other side, the Kjeldahl digestion rack is located. Gas, electricity, vacuum, and water are provided in the hood and may be controlled from without as well as from within.

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RECEIVED October 21, 1938.



MICRO-KJELDAHL DISTILLATION APPARATUS WITH WATER-COOLED STEAM-GENERATING FLASK

After water is added to the steam-generating flask, the liquid in the vacuum jacket will be immediately transferred to the discharging flask. The liquid can then be emptied into the drain. Pumice stone is an excellent material to prevent bumping in the generating flask.



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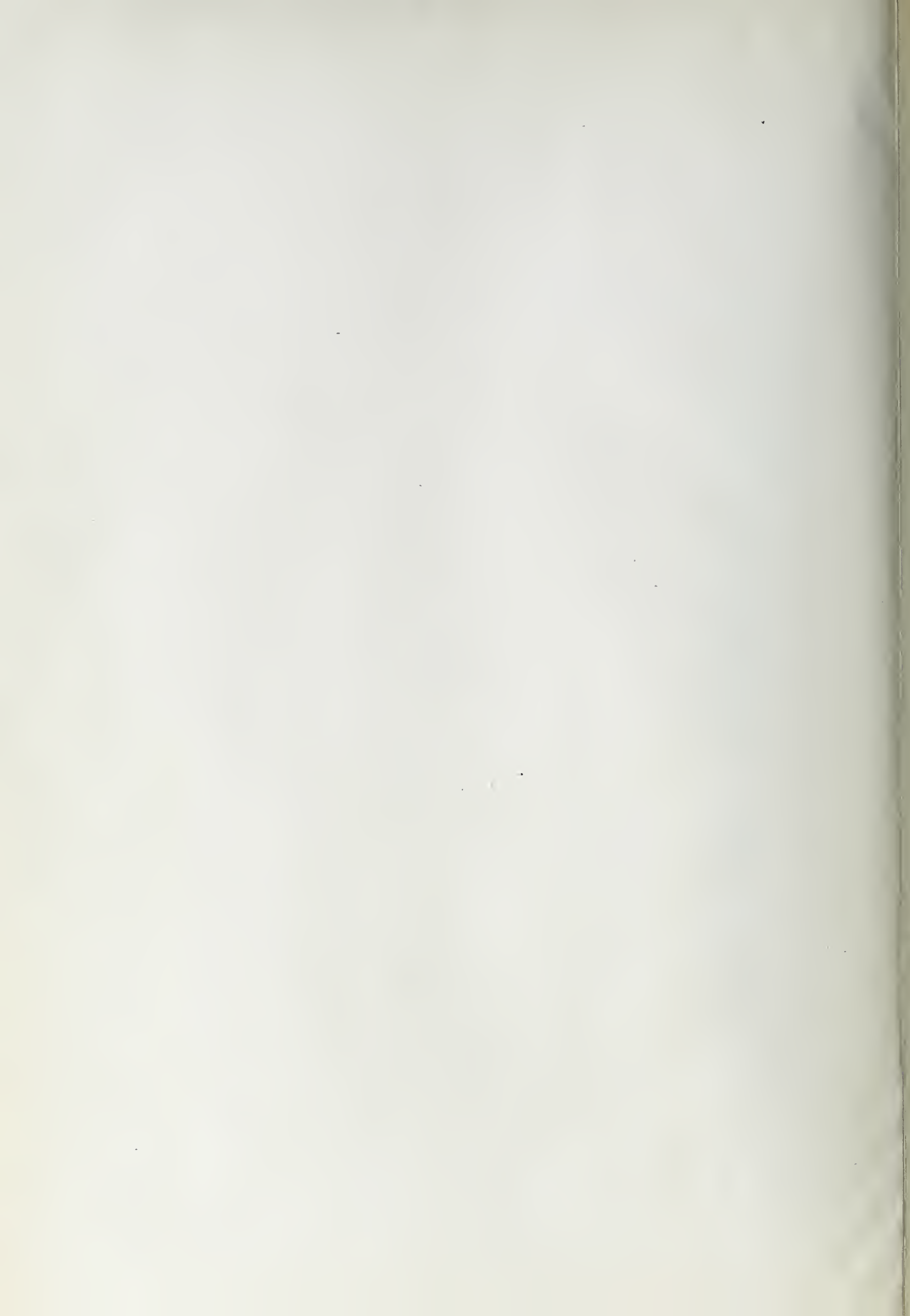


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